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# JPRS Report

# Science & Technology

## Japan

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JPRS-JST-90-037

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8 AUGUST 1990

## New Approaches to Material Development

*90FE0124A Tokyo PROMETHEUS in Japanese Mar-Apr 90 pp 9-11*

[Article on Basic and Specific Policies for Material Science and Technology, written by the Material Development Promotion Office, Research and Development Bureau, Science and Technology Agency]

[Text] The emergence of new oxide superconductivity toward the end of 1986 not only gave significant confidence and bright prospect to those of us who were directly involved in material science and technology, but also was an epoch-making discovery that made people all over the world have limitless dreams and hopes for the progress of science. At the same time, this discovery gave a meaningful clue for the significance and essence of basic research. The discovery is also believed to visibly impact on the future science and technology policies of Japan. The importance of original and creative basic research has been much stressed in the field of material science and technology. In this article, we shall discuss the basic and specific policies on material science and technology, while briefly discussing the overall development of basic research.

### CST Sets Basic Policies for Material Science and Technology

Japan's material science and technology is promoted in accordance with the basic policies established by the Council for Science and Technology (CST), the highest organization to deliberate on the government's science and technology policies. The Science and Technology Agency (STA) is in charge of planning, designing, promoting and coordinating the science and technology policies in the field of material science and technology. From this standpoint, STA is involved in planning and designing various policies as the secretariat for CST and the Council for Aeronautics, Electronics and Other Advanced Technologies (CAE). STA also handles businesses involved in the Prime Minister's approval on the plans, if necessary. Furthermore, as will be discussed later, STA handles business concerning the Science and Technology Promotion Coordination Fund in order to coordinate overall science and technology, and STA carries out important comprehensive research in the material science and technology field.

**Fundamental Views:**

*The material science and technology field is the driving force for technological revolution aiming at developing the 21st century's human society.

*With emphasis on basic research, the creation of materials having revolutionary functions as well as the sophistication of application technologies will be targeted.

*Contribution to the international community will be aggressively pursued.

#### (1) Various Policies Based On Reports by CST

Concerning the material science and technology field, CST issued the Report No. 14 (August 1987), titled "The Basic R&D Plan concerning Material Science and Technology."

In this report, CST lists four specific priority R&D targets: (1) search for new phenomena and theoretical clarification of various phenomena, (2) creation of revolutionary substances and materials, (3) development of material technology corresponding to needs, and (4) development of common and key technologies. The report also points out the need for the following four items in promoting R&D in this field: (1) personnel training and securing, (2) ample R&D funding, (3) information exchange promotion, and (4) the promotion of international exchange and cooperation. In October 1987, this report was approved by the Prime Minister as "The Basic R&D Plan concerning Material Science and Technology." In addition, CST's Policy Committee compiled and published a report titled "The Basic Promotion Plan for the Superconductivity Research Policies," (report on the November 1987 round-table discussion meeting concerning superconductivity) to indicate the basic views on related policies. Material science and technology R&D is advanced on the basis of these views.

#### (2) Report by CAE

CAE, led by its Material Technology Committee, deliberates on various topics and submits its reports to the Director-General of STA. Thus far, the following reports have been submitted: (1) the report (August 1980) in response to the deliberation topic No. 5, "Promotion Plans for Overall Research concerning Extreme Science and Technology and Associated Material Science and Technology;" (2) the report (September 1984) in response to the deliberation topic No. 7, "Promotion of Comprehensive R&D concerning the Creation of New Materials based on Material Design Theories;" and (3) the report (March 1986) in response to the deliberation topic No. 9, "Priority Topics and Their Promotion Methods for the Sophistication of Instrumentation and Control Technologies concerning New Material Development." Upon receipt of these reports, related R&D projects have been aggressively pursued.

Recently, in November 1989, CAE submitted a report on the so-called "intelligent materials" in response to the deliberation topic No. 13, "Promotion of Comprehensive R&D concerning the Creation of New Substances and Materials Capable of Intelligently Responding to Environmental Conditions and of Manifesting Functions." We refer you to "Zadankai (Round-Table Discussion" for the detail of this report.

### STA's Enforcement Policies and R&D

As mentioned before, STA plans, designs, promotes and coordinates overall business matters for the material science and technology policies. In addition, STA and

organizations under its jurisdiction are enforcing policies and carrying out R&D concerning material science and technology. For example, in May 1988, STA inaugurated the new superconductor research system, called "the superconductor research multi-core project," which is tackled by the entire agency organization. Each of the organizations under STA's jurisdiction is pursuing R&D concerning material science and technology either under a specific system or within an R&D project. These organizations include national research institutes, such as the National Research Institute for Metals, the National Institute for Research in Inorganic Materials and the National Aerospace Laboratory, and special corporations, such as the Institute of Physical and Chemical Research, Research Development Corp. of Japan, the Japan Atomic Energy Research Institute, Power Reactor and Nuclear Fuel Development Corp., the National Space Development Agency of Japan, the Marine Science and Technology Center and the Japan Information Center of Science and Technology.

**STA's Overall R&D Program**

Under the system described above, STA is advancing material science and technology. Given below is the more specific explanation of the science and technology promotion coordination fund and the superconductor research multi- core project.

**(1) R&D Promotion with Science and Technology Coordination Fund**

The science and technology promotion coordination fund was established in FY81 as a national policy to enforce the comprehensive promotion coordination of key research projects in accordance with CST's policies. One of the government's key policies has been to establish a science and technology nation. The fund was established so that CST, the highest organization to deliberate Japan's science and technology policies, could play a leading role in enforcing science and technology policies by displaying the function of overall coordination based on its high-level knowledge and vision.

Under this system, (1) integrated research, (2) international floating basic research, (3) individual key international cooperative research, (4) surveys and analyses, and (5) emergency measures are carried out.

In FY89, there were nine research topics in the field of materials under the integrated research; they included "research concerning measurement, evaluation and control technologies of elemental material functions in ultra-micro-regions," and "research concerning database construction for superconductor R&D."

All the integrated research topics in the field of material science and technology from FY80 are listed in Table 1. Of these, "research concerning key technologies for functionally gradient material development to alleviate thermal stress" is discussed in a separate article.

**Table 2. Research Cores**

| Target Area | Research Core | Core Organization |
|---|---|---|
| Theory and Database | Theory | National Research Institute for Metals |
| | Database | National Research Institute for Metals |
| Synthesis and Structure Control | New Material Search | National Institute for Research in Inorganic Materials |
| | Raw Material Control | National Research Institute for Metals |
| | Thin Film Formation | National Research Institute for Metals |
| | Single Crystal Formation | National Institute for Research in Inorganic Materials |
| | Microscale Fabrication | Institute for Physical and Chemical Research |
| | Composite Formation | National Research Institute for Metals |
| | Space Environment Utilization | National Space Development Agency of Japan |
| Analysis and Evaluation | Superconducting Property Evaluation | National Research Institute for Metals |
| | Crystalline Structure Analysis | National Institute for Research in Inorganic Materials |
| | High-Sensitivity Composition Analysis | Institute for Physical and Chemical Research |
| | Radioactive Irradiation and Analysis | Japan Atomic Energy Research Institute |
| | Measurement and Analysis Support | Material Science and Technology Promotion Foundation, Inc. |
| Technology Expansion | Technology Expansion | Research Development Corp. of Japan |

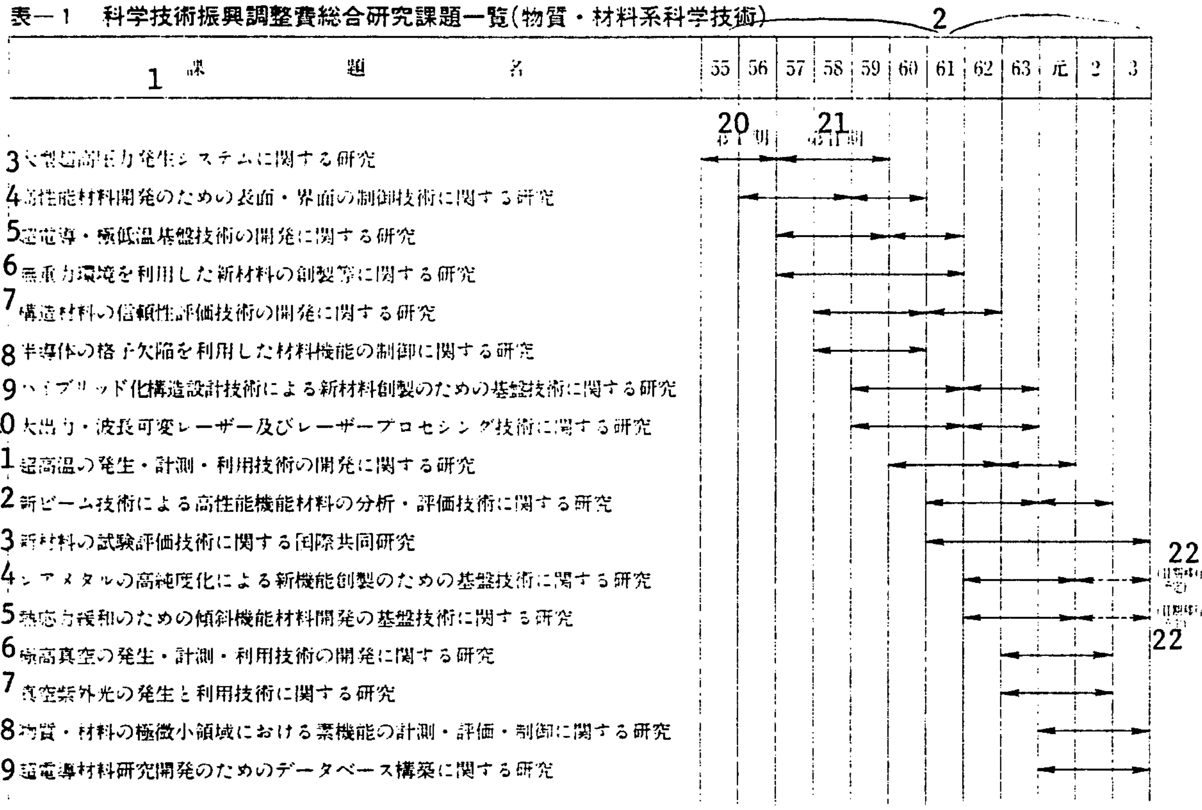


**Table 1. Summary of Integrated Research Titles under Science and Technology Promotion Coordination Fund System (Material Science and Technology Field Only)**

Key:—1. Title—2. These are FYs: 55 should be changed to 80, 56 to 81, etc., through 63 to 88, which should be followed by 89, 90 and 91.—3. Research concerning large-scale superhigh pressure generation system—4. Research concerning surface and interface control technology for high-performance material development—5. Research concerning the development of superconducting and cryogenic key technology—6. Research concerning the creation of new materials in a microgravity environment—7. Research concerning evaluation technology development for structural material's reliability—8. Research concerning material function control by using semiconductor's lattice deficiency—9. Research concerning key technology for new material creation by hybrid structure design technology—10. Research concerning large-output, wavelength-variable laser and laser processing technology—11. Research concerning the development of superhigh temperature generation, measurement and application—12. Research concerning analytical and evaluation technologies for high-performance functional materials by new beam technology—13. International cooperative research concerning testing and evaluation technology for new materials—14. Research concerning key technologies for new function creation through rare metal purity improvement—15. Research concerning key technologies for functionally gradient material development to alleviate thermal stress—16. Research concerning the development of ultrahigh vacuum generation, measurement and application technologies—17. Research concerning vacuum ultraviolet light generation and application technologies—18. Research concerning measurement, evaluation and control of elemental material functions in ultramicro-regions—19. Research concerning database construction for superconductor R&D—20. First phase—21. Second phase—22. (Expected to advance to second phase)

### (2) Superconductor Research Multicore Project

Since the discovery in 1986, the critical temperatures of new oxide-base superconductors have exceeded the liquid nitrogen temperature of 77K, reaching an approximately 120K level upon further discoveries of new bismuth-base and thallium-base materials. Moreover, a totally different type, new neodymium- base material was also discovered to raise our hopes for new materials that will bring technological revolution in the 21st century.

R&D on these new superconductors is still at a fundamental stage, and many problems must be solved in the future in order to establish these materials as a practically useful material. The "Superconductor Research Multicore Project" is a project that will aim at paving the

road for practical applications of the new superconductors and contributing to the advancement of global R&D, and multifacetedly promote fundamental and key research concerning new superconductors. To do so, the project will establish R&D potential cores at national research organizations and special corporations, and promote flexible joint research projects, which focus on researchers regardless of nationality and their affiliate, such as industry, academe or government, as well as researcher exchanges and information exchanges. As shown in Table 2, the project involves approximately 200 researchers at 15 research cores.

## Functionally Gradient Material R&D

*90FE0124B Tokyo PROMETHEUS in Japanese Mar-Apr 90 pp 4-5, 12-13*

[Part I, pp 4-5, is the "Functionally Gradient Materials" portion of an anonymous article titled "New Materials in the Dreamworld." Part II, pp 12-13, titled "Functionally Gradient Material Development Project," was written by Masayuki Niino, Chief, Rocket High-Altitude Performance Research Laboratory, National Aerospace Laboratory, Science and Technology Agency]

[Text] **Part I**

### New Concept on Functional Gradient

Completely new materials called functionally gradient materials have been conceptualized in Japan, and their development projects are in progress.

For example, a space plane (shuttle) in a long atmospheric ultrasupersonic flight (at approximately Mach 5) requires stability against intense heat and durability for several hundred times such a flight. Moreover, the fuselage materials must withstand an environment that will create large internal temperature gaps. Therefore, attempts have been made to produce materials with stability against thermal stresses through synthesis with the optimal distribution of composition and structure in the interim layer between the heat-resistant ceramics used for the high-temperature side and the thermally conductive and functionally strong metallic materials used for the cooling side.

Many research accomplishments concerning such synthesis technologies have already been published. Based on results of basic studies on the physical vapor deposition method by the National Research Institute for Metals and the chemical vapor deposition method by the Metal Research Institute at Tohoku University, Sumitomo Electric Industries, Ltd. successfully synthesized a functionally gradient material by a physicochemical vapor deposition-fusion method. This material forms a Ti-TiC-base compositional gradient layer on the low temperature side and a C-SiC-base compositional layer on the high temperature side, with a C/C composite used for the matrix.

Nippon Kokan K.K. developed a thin film layering method, with which thin film multilayers of mixed raw materials of ceramics and metals were made, and established a production method for small and flat functionally gradient materials that would neither warp nor crack.

Japan Steel Corp. developed a four-port reduced-pressure simultaneous sputtering device which uses one plasma gun to sputter powders from four directions via the reduced-pressure plasma sputtering method, and successfully synthesized monolithic compositionally gradient films with few micropores.

The Government Industrial Research Institute, Tohoku, developed an automatic multilayer packing device and a static pressure compression process, and simultaneously synthesized and shaped a functionally gradient material that was large, complex-shaped, monolithic and crack-free, by ignition-synthesizing a mixture of metal and non-metal powders under static pressure. This self-heating reaction method was based on results of basic research done at the Industrial Science Research Institute, Osaka University.

Today, by manipulating these original synthetic technologies, R&D is pursued to produce large-sized and complex-shaped functionally gradient materials.

**Part II**

### Functionally Gradient Material Development Project

### To Challenge New Space Era

Space planes (space shuttles), which are now in the limelight worldwide, need long ultrasupersonic flights (approximately at Mach 5) in the atmosphere because they make horizontal take-offs and landings just as conventional aircraft do.

Therefore, their fuselages and engines receive extreme heating and attain a superhigh temperature (approximately 1,700°C), requiring cooling by liquid hydrogen, which is the fuel. The planes are further required to be able to endure several hundred flights. That means that the planes need a heat- shielding super-heat resistant material that can be used in a high-temperature environment where a large inner temperature gap is created.

Based on these requirements, the concept of totally new materials called "functionally gradient materials" was born in Japan.

### Concept of Functionally Gradient Materials

The concept of a functionally gradient material for alleviating thermal stress is illustrated in the schematic diagram (Figure 1). Materials which are resistant to thermal stress are to be synthesized by having a ceramic material for the surface in contact with high-temperature gas at several thousand °C, a metallic material for the cooling surface to impart good thermal conductivity and

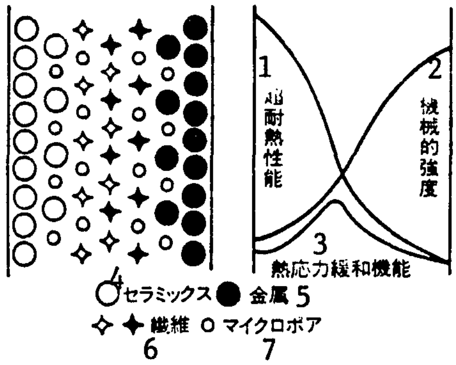


**Figure 1. Manifestation of Functional Gradient**

Key:—1. Super heat resistant capability—2. Mechanical strength—3. Thermal stress alleviation function—4. Ceramic material—5. Metallic material—6. Fibers—7. Micropores

mechanical strength, and an intermediate layer with an optimally varying composition and/or structure.

These materials, that are obtained with a functional gradient by controlling the continuous distribution of constituent elements (metals, ceramics, plastics, fibers and micropores) to cope with an environment where they are to be used, have been named "Functionally Gradient Materials (FGM)." This concept of FGM can not only offer a means of solving many problems occurring at interfaces, but it also can offer potentially limitless possibilities for the compositional gradient itself to manifest a new function in the material. Thus, FGMs are expected to be used in wide-ranging areas, including aerospace materials, the nuclear fusion field which requires heat resistance and radioactive ray resistance, the electronics field which requires electric and optical characteristics, and the medical field which requires biocompatibility.

**Introduction of FGM Development Project**

In FY87, the project with the title, "Research concerning key technologies for FGM development to alleviate thermal stress," was initiated under the Science and Technology Promotion Coordination Fund System. As shown in Figure 2, the project has been advanced under close cooperation among its three divisions of material design, structure control and characteristic evaluation, and a database. The project's ultimate objective is to develop a material that can withstand the highest surface temperature of 1,700°C and an internal temperature drop of 1,000°C. The target for the project's first phase, the three years from FY87, is to synthesize a small test piece one to 10 mm thick and 30 mm in diameter. The target for the second phase, the two years from FY90, is to synthesize a shell sheet of the same thickness and 300 mm square.

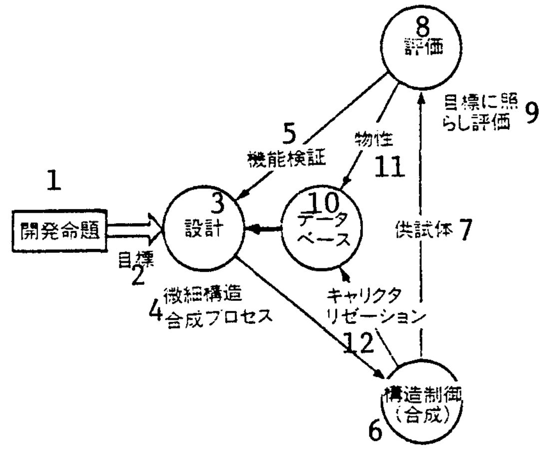


**Figure 2. R&D System**

Key:—1. Development Proposition—2. Targets—3. Design—4. Microstructure, Synthesis Process—5. Function Verification—6. Structure Control (Synthesis)—7. Test Samples—8. Evaluation—9. Evaluation against Targets—10. Database—11. Physical Properties—12. Characterization

**Research Progress Status**

The Material Design Division performs material design by a new computer- assisted design technique; based on that design guidelines, the Structure Control Division test-produces FGMs with optimal compositional distribution by freely using new synthetic methods; and the Characteristic Evaluation Division conducts performance tests on the test-products in a simulated extreme environment which space planes are expected to encounter, by using a high- temperature drop basic evaluation device at the National Aerospace Laboratory. (Refer to pp 4-5 of this magazine.)

## Intelligent Material Development

*90FE0124C Tokyo PROMETHEUS in Japanese Mar-Apr 90 pp 3-4, 14-22*

[Part I, pp 3-4, is the "Intelligent Materials" portion of an anonymous article titled "New Materials of the Dreamworld." Part II is on the round- table discussion by four experts (Mr. Toshinori Takagi, Professor Emeritus and Director, the Ion Engineering Research Institute; Mr. Teruo Okano, Assistant Professor, Tokyo Women's Medical College, and Associate Professor, University of Utah; Mr. Junzo Tanaka, Chief Researcher, The Tenth Research Group, National Institute for Research in Inorganic Materials, Science and Technology Agency; and Mr. Takayuki Shirao, Material Research Coordinator, Material Development Promotion Office, Research and Development Bureau, Science and Technology Agency) on the topic of "Report on Intelligent Materials by the Council for Aeronautics, Electronics and Other Advanced Technologies"]

[Text] **Part I**

**Expectation for Quasicrystals**

Previous materials have been studied from the mutual relationship between the structure and the properties (functions). Intelligent materials, the materials of the 21st century, are new materials that, on a higher level than the so-called highly functional materials, will break ground for a new scientific discipline in which a new concept of information (molecular communications) is added to the structure and function, as shown in diagram on p 3 [not reproduced].

The intelligent materials by themselves respond to an outer environment, change their structure, and perform an appropriate function. In other words, the materials, as a molecular device, can decipher signals they themselves have detected, draw a conclusion, and initiate an appropriate action. They are expected to create new application fields and industries.

If sophisticated intelligence is to be imparted to a ceramic material, there are many fundamental topics that need to be physically and chemically clarified and investigated. One example of these topics is the quasicrystal (see illustrations on p 3 [not reproduced]) that does not exist in nature under normal circumstances. The quasicrystal has a periodic structure (psudoequilibrium) of atomic arrangement in the five or six-dimensional space, having a higher dimension than the normal three-dimensional space. As shown in the diagram on p 3 [not reproduced], the crystalline structure does not appear to have periodicity in the three-dimensional space. Although the theory on characteristics of quasicrystals has not been established, they are expected to show strange magnetic behaviors due to their special structure.

**Part II**

Shirao—On 30 November 1989, the Council of Aeronautics, Electronics and Other Advanced Technologies compiled a report on the so-called intelligent materials. Because we had expected to find a foothold for new material development from this report, we were greatly encouraged by the report which was certainly not an easy task.

First, we would like to ask Mr. Takagi, who was the committee chairman for the report compilation, to discuss the main points and the new characteristics of the intelligent materials.

Takagi—In the first place, I would like to start with the background as to how the Council had decided to prepare such a report.

Thus far, Japan has made tremendous achievements by importing good ideas and inventions from other countries and improving their performances. This, no matter how little information available.

However, as Japan has been urged by other nations of the world to be more responsible and confident as one of the global powers, Japan needs to advance new sciences and technologies based on its own ideas. Or else, it faces the consequence of being accused for the so-called technological piggyback ride. From now on, we must start with an expression, "So and so denotes—," instead of "So and so is—." In other words, Japan must clearly understand whether such a new concept truly exists, and if so, what kind of concept it is. Moreover, the concept must be commonly understood worldwide. So, you can see the job of defining the concept of intelligent materials from these standpoints was almost as difficult as a brand new experience.

Consequently, the report this time presents a conclusion of how to think, which is different from the previously customary conclusion of recommended hardware (things) to produce a given item. Thus, while previous reports began traditionally with the introductory first chapter, followed by the second and third chapters containing the main parts of the reports, in this particular report, the third and fourth chapters, previously having dealt with specifics, have only few pages. This is the extremely unique feature of this report, and it also reflects its background.

First of all, materials can be made functional or intelligent. Then, what is the difference between highly functional materials and intelligent materials?

In early attempts to develop highly functional materials, more or less passive functions, such as friction resistance and high-temperature resistance, have been targeted. Later, the targets have shifted to active functions, such as the conversion of solar ray to electric energy. However, now we are talking about, as well as we want to create functions to automatically detect and decipher signals and to automatically start actions.

Previous materials have possessed various scientific and physical characteristics (physical properties) and functions, and more highly functional materials have had more of the characteristics and functions. This time, we want to add a new concept of information to these highly functional materials to have them think and draw conclusions by themselves (Figure 1).

In biological organisms, such as humans, there are intelligent materials, including the nerve cells (neurons), which handles information processing, and the contact points (synapses) performing information transmission. Thus, we want to simulate genetic engineering in the world of lifeless materials to scientifically create materials that have never existed in this world, to impart intelligence to these materials, and to systematize these materials to make them capable of an extremely high degree of recognitions and actions.

Briefly stated, the idea behind the development of intelligent materials is that we want to realize our ambition to make machines that are friendly to humans through these materials.

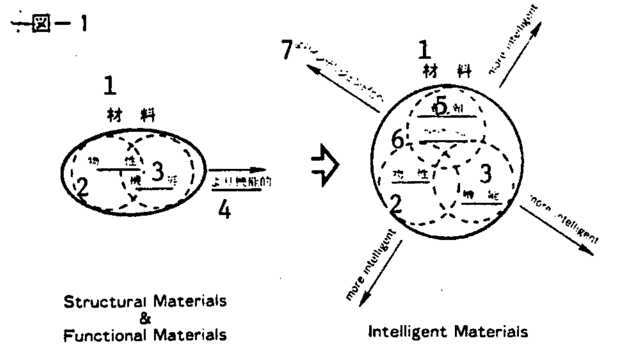


Figure 1

Key:—1. Material—2. Physical Properties—3. Functions—4. More Functional—5. Information—6. Software System—7. More Intelligent

Shirao—It was indeed a rare form of our government's report that advocated an idea. At any rate, it was an extremely novel report.

The fact that Japan has proposed such new materials should deserve some appraisals from abroad as well as from within Japan. Mr. Okano, you were doing research in the U.S. for a long time. What is your thought on this?

Okano—I don't think the concept of material has been clearly understood in Japanese society.

I believe, a material is a device, regardless. Among many research projects carried out thus far, those projects dealing with systems, i.e., how to combine elements, and how to organize a highly functional system, have led Japan's high-tech industries. However, the development of devices that have converted vacuum tubes to transistors and super-LSIs, has caused significant breakthroughs.

Probably, Japan was not accustomed to such a move to consolidate works done in various fields into this new concept. In Europe and the U.S., a tremendous power was used for this type of work on a national level to create new fields. Therefore, they have an understanding that they must powerfully advance such new projects. Here, I sketched an idea diagram called "Intelligent Material" (Figure 2). In short, although the structure and function have supported previous materials, materials are used in an environment where all kinds of molecular communications (molecular exchanges) are taking place. Therefore, it becomes important to scientifically understand a problem of intermolecular communications between a material and an environment and to incorporate molecular devices, i.e., associated functions, into the material as a system. I think, this material is an intelligent material.

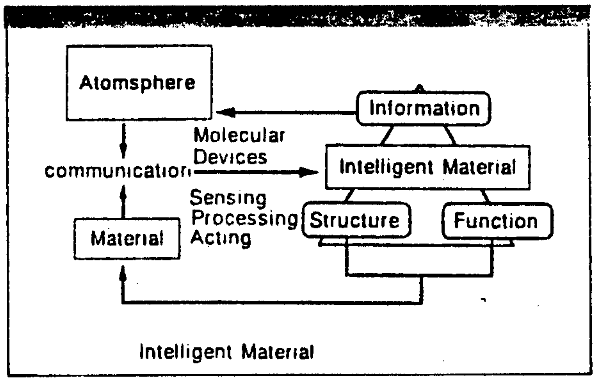


Figure 2

Takagi—In our engineering community, we separate materials from devices. A device is a device, and not a material.

Thus, we are already on the verge of developing an intelligent device, called a three-dimensional structure device. It has a sensor layer on its top, an intermediate layer of logic circuit, and a memory layer at the bottom. The device senses signals at the top layer, compares them with signals already inputted in the bottom layer, and makes decisions by the logic circuit.

Let the thickness, interfaces and others of the idea of having such three layers be reduced infinitesimally, and we have an intelligent material. Furthermore, the number of layers can be three or five, and we shall be able to express more sophisticated functions than what we know today.

Shirao—Mr. Tanaka, you deal with inorganic materials at the National Institute for Research in Inorganic Materials. My humble impression tells me that you are considerably away from the concept of intelligent materials. How do you see these intelligent materials from the standpoint of inorganic materials?

Tanaka—I am afraid, biological systems and ceramic systems are quite different from each other. The most obvious difference is the following. In biological systems, when an enzyme is found in a living body, we have a built- in model for studying the mutual relationships between the enzyme's oxygen and a sophisticated molecular or atomic structure, and between the amino acid sequence and the function of the enzyme. On the other hand, in many instances, there are no models for ceramic system, when an intelligent material is to be developed.

However, I believe that in principle, more than one function can be built in a ceramic material. For example, one wants to build another function into a material that already has a function. To do so, inorganic materials will be combined with highly selective enzyme analogs through the incorporation of the boundary region between inorganic and organic compounds or an enzyme in a living body. I think, we might be able to develop intelligent ceramics fairly soon, when viewed from the

standpoint close to the living body or close to the organics, as mentioned above.

Takagi—I'm sure that the living body and the inorganics are far apart. However, because they are different, if we can find a hint or two from the living body, we will be happy to take in the idea. In other words, those working with ceramics, metals or functional devices would like to aggressively adopt whatever models the living body can demonstrate.

As we think that way, I realize that we, people with an engineering training, are least familiar with some of the living body's properties, such as the self-restoration function, life-predicting function and learning function, that respond sensitively to the time coordinate, and with the creation of these properties.

Tanaka—You think that biological algorithm (rule of thinking) could be adopted for ceramics. I think you are right, and we also think it should be possible to do so. Enzymes are actually a series of approximately 10,000 amino acids. Even if we want to simply seek the relationship between the enzyme's function and structure, or the sequence of molecules and atoms, the enzyme's code theory consists of an infinite number of combinations that cannot be decoded today. However, in fact, biotechnologists are steadily clarifying some of the relationships. I feel, their view on the material's algorithm might be well applicable for ceramics.

Takagi—I'm sure you feel that way. However, during the course of applying the algorithm, one must consider a possibility to form ceramic-metal, or ceramic-organic material composites, and one must also think about technological control at the atomic and molecular level, as mentioned earlier.

Okano—In biotechnology, it is comparatively easy to identify the function and the structure, and the simulation of models has been studied in depth in the biomimetic field. However, one material has not only one function but may have four functions altogether. Today, it has never been clarified for such situations where a communication action has started in a molecule, and not only one function, but the second and the third functions have all been triggered. Yet, the biomimetic technique cannot deliver a material desired, unless all the mechanisms involved are understood. If that is the case, we should use a new approach to clarify a biological complexity set in a completely different environment, and at the same time, to incorporate the complexity into material design.

Takagi—I think there are two ways to do that. One is to use the complexity in a living body. The other is to create a brand new complexity based on clues taken from the living body as observed by our own eyes.

Tanaka—You are exactly right. I think, one of the important aspects of biological materials is the mutual action between the body and ceramics, as seen in the bones' functions. The bones have the physical functions of supporting the body, protecting the organs and offering the blood-producing sites, and in addition, the bones act in harmony with the body to do self- restoration and to adjust the concentration of inorganic ions contained in the bone material in order to maintain homeostasis in body fluids.

Today, because problems are being solved for bone-functional materials, it is imminent for the materials to be qualified as an intelligent material.

Takagi—When you say an intelligent material, which is, let's say, a bone, do you mean that the bone can be made to know that sometimes it should not adapt immediately to muscles, or in other times it should never adapt to muscles at all, or it should grow, as a natural bone, by absorbing calcium from the body?

Tanaka—Yes, I do. In that sense, I think, the bone-functional materials might become a model case for the mutual action between ceramics and the living body.

When we check individual ceramic and inorganic materials, we find the sensor function, which senses environmental changes, i.e., changes in surrounding conditions such as magnetic field and temperature, already in practical applications, and we also find an active sensor in the actuator used for scanning tunnel microscopes (STMs). However, at the current stage, each individual material has a high-degree function, which cannot be composited. If we can develop algorithm to incorporate more than one function into one material, I think, intelligent materials can be made from ceramics in the future.

Shirao—Well, our discussion appears to be approaching the core point. I think we can easily imagine where Mr. Okano's DDS (drug delivery system) will be useful. Mr. Okano, I think we would be more interested in your system, if you would please talk about technical possibilities, including your dream of possibly developing a certain intelligent material.

Okano—If we take a readily comprehendible example, today's artificial organs do nothing but physical work.

As you know, although called an artificial organ, the artificial liver is acting as a detoxifying agent, which is only one of many liver functions. The artificial kidney is also performing only one function of filtering unwanted materials from the blood.

The pancreas secretes a peptide called insulin, signaling sugar intake for the body by lowering the blood sugar level. When insulin is used for treatment, hypoglycemia arises. Therefore, insulin is administered for the treatment, while monitoring the blood sugar level. In fact, an artificial pancreas system is soon to be developed for hospital use, and it works as follows. Information obtained from a glucose sensor is first dropped to the elementary particle level and then converted to electrical signals. Using a computer with stored data on a patient's daily blood sugar variations, e.g., how much his blood

sugar level increases after a meal, the signals are compared with calculated values and relayed to a syringe pump, which administers a computer- determined amount of insulin to the patient.

However, our pancreas is just a small, racemose gland. If, right now, this gland can be artificially realized from an intelligent material, the material itself must detect the glucose concentration, and based on that, secrete a calculated amount of insulin. From the technological standpoint, the artificial pancreas has come close to its development goal through the ingenious use of polymers. I hope, after explanations like this, a molecular device becomes more readily understandable.

Takagi—Although called device, it is rather a material, isn't it?

Okano—Currently, our laboratory is developing a temperature-sensing gel that changes its form with the temperature.

If the gel contains an analgesic, the gel will deliver the drug or stop delivering depending on the temperature. In other words, the gel can be used as a complete on-and-off switch. Moreover, based on the external temperature change, the drug dose can be accurately determined. Ideally, the analgesic should be administered when a patient has fever, and the drug should be held in the gel when fever is gone.

Takagi—We can extend this discussion to our daily living. For example, as a starter, how about a window pane that, regardless of the intensity of outside light, can always create inside conditions exactly as preset? This is not necessarily an impossibility, if changes can be made by the intensity of incident light.

A while ago I mentioned the life-predicting function. What do you think of an insecticide or a germicide that changes its color when it loses efficacy? In a sense, this can be regarded as a sort of prototype of life prediction. There are other useful phenomena in more familiar places; for example, scratches on Alumite (anodized aluminum) are gradually healed by using its growth through absorption of oxygen from air.

A material itself of ladies' dresses would be equipped with a solar battery- like action, so that the wearer could input her desired humidity and temperature and the dress material would cool itself when the set temperature is exceeded, and the material would warm itself when it becomes cooler outside. This should be a sizable R&D field on intelligent cloths, shouldn't it? We could also develop walls, specifically intelligent walls that would absorb moisture when it becomes humid in a room and would desorb moisture when humidity goes down. These walls could also control temperature. Thus, I think, we can let our imagination run in various directions.

Tanaka—As I listened to you, I also got some ideas.

The most serious shortcoming of ceramics is low reliability due to brittleness. If a material could predict its own life by itself, its reliability would improve. If physical property changes of such a material could be monitored, life prediction could be realized in various forms.

If I think of a wall, that, on account of phase transition, would generate heat and become warmer at a certain temperature, and conversely, would absorb heat and cool itself when the temperature increases, I begin to wonder if there would perhaps be quite a few intelligent-type materials among ceramics.

Takagi—Another characteristic of the report, we are discussing, is that it is the result of systematic and comprehensive examination of various concepts on intelligent materials in an extremely wide-ranging fields from medicine to polymers, to ceramics and to electronics. One very important meaning of this report lies in the fact that it was based on thinking by a variety of people, unlike previous reports which were based merely on individual thinking within his experiences and domain.

Shirao—That is exactly correct. Toward the final stage of compiling the report, we had heated discussions on where we were going from there.

Of course, everyone recognized the need of more basic research for the future new material development, and at the same time, we thought that there ought to be many studies on key points in order to uncover the so-called intelligent functions, such as stable state, pseudoequilibrium and disorder.

In this report, we find a long and unique foreign word "mesoscopic." This word itself appears to have become hackneyed among researchers. However, as a rule, phenomena become more clearly understood, as one approaches closer and closer to the molecular and atomic levels. Conversely, for the creation of intelligent materials, one must first find unique phenomena or mechanisms. Therefore, the work "mesoscopic" will acquire more flavor of reality, if one tries to discover the phenomena at this mesoscopic level and realize them in terms of plural functions in those materials we have been discussing. In the future, we should try to define such an opening more clearly. Or, I wonder if there should be some kind of axis, like the opening somewhere in a new kernel or organization which researchers might want to organize.

Takagi—At any rate, what we want to do in any R&D situation is to develop human-friendly products, isn't it?

Today's personal computers will do jobs for us only after our nudging with immense patience, right? We want to create machines that could perceive our feelings a little more.

Therefore, materials themselves need to be made intelligent, so that when a system is built from them, it will be as sympathetic toward us as possible. Of course, if the system is too aware of human feelings to think, "Since we don't get along, I will quit working," that would be a

disaster. (Laughs) I believe, the ultimate objective is to develop whatever it is that sympathizes with human feelings and is easy to use.

In order to achieve the objective, we must develop materials, the individual constituents and elements of a system, that can make judgments by themselves. Thus, when a system is built, it will have even more sophisticated functions.

I think, that is our ultimate goal.

Tanaka—Recently, we had the Ninth Science and Technology Forum in Tsukuba. There, a discussion took place on the argument that one must think new robotics, rather than only robotics, in robotic engineering. Thinking that this discussion was similar to the popular topic of imparting intelligence to materials, I listened carefully with a notion that the discussion might really be on creating intelligent robots.

Three elements were discussed. One was to analyze human functions. The second was to newly establish human functions within a robot. These two alone were said to be insufficient. What we need as the third element, it was told, was to secure harmony between human and the robot.

New robotics seems to try to impart survival capability, thinking capability to cope with nature and learning and self-organizing capability in robots. However, more importantly, models with integrated senses are sought in new robotics.

For example, we, as a family, enjoy regular dinners at home, and the dinners do not necessarily have to be French cuisine. However, if we happen to eat a dinner with someone we dislike, we don't enjoy the dinner even if it is French cuisine. This is perhaps because all the senses, including the senses of smell and of taste, react with each other.

When we view such a sense-integrated model from the material standpoint, it would not be sufficient for the material to have only the function as a sensor. The material must be able to automatically process information obtained from the sensor and synthesize and perform the result of mutual actions between the senses of smell and taste, for example.

In that sense, I wondered if we need to perceive an intelligent material as a more human-friendly material.

Okano—We want to develop a material that is not a one-dimensional sensor but can judge by simultaneous processing multi-dimensional information.

To realize that, I think, it would be ideal if we could first build a concept based on the materials that can respond to only one information and then create a totally new system out of intelligent materials that are capable of processing multi-dimensional information, as you just mentioned.

Takagi—Although the report, in a straightforward fashion, talks about materials equipped with three functions of sensor, processor and actuator, things do not progress as non-continuously and immediately as the report sounds. In this way of thinking, it would be quite satisfactory if only two out of the three functions have been successfully developed or if more than one function, though almost every one is the sensor function, have simultaneously been processed. In that manner, we climb stairs one step at a time. I think, that is the way to always look at things.

I might add that in compiling this report, we were fully aware of the closeness of the international society, by which the report must be acknowledged. Mr. Shirao, wouldn't you say that it was epoch-making to have had international research gatherings before the report draft was completed?

Shirao—Yes, I would.

Takagi—This time, things went extremely well. The journal "Nature" quickly reported on our research gatherings on intelligent materials. In 1990, a new journal, "Journal of Intelligent Material Systems and Structures," debuted in the U.S. In March 1990, a U.S.-Japan seminar on intelligent/smart materials is to be held. So, the interest is keen worldwide.

In the U.S., the terminology of "smart materials" had initially been favored. However, because frequent and active discussions on "intelligent materials" began in Japan, the journal took up the title, "Intelligent Material Systems."

We would be extremely thankful, if everything works out as nicely as has done so thus far.

Shirao—As you are quite aware as you have discussed here, we have previously owed much to research achievements abroad. In order to change from that era, we must start from concept building at all cost to gain recognition. In that sense, could we say that Japan is getting closer to be the front runner not only in the material field but also in other fields?

Takagi—Yes, we could.

Right now, Japan needs to establish the new concept, as mentioned at the beginning of this discussion, of starting with "So and so denotes—" instead of "So and so is—."

In the past, Japan did not have opportunities to discuss, and Japan did not discuss the committee on "how to be" and the concept establishment. Because Japan did not really mind not doing the discussions, it was able to catch up, at any rate, with other advanced nations in such a short time.

Therefore, I am not suggesting that Japan didn't do right in the past, but I think that it will be very important for Japan to carry out the above- mentioned concept establishment and to contribute to the world for the purpose

of smoothing international exchanges and establishing a harmonious international environment.

Shirao—Gentlemen, thank you very much for taking time out from your busy schedules.

## New Materials From Hybridized Structure Design Technology

*906C7505A Tokyo in Japanese Oct 89 pp 1-178*

[Report by the Research and Development Department of the Science and Technology Agency: "Research on the Basic Technology for Creating New Materials Using Hybridized Structure Design Technology", under the FY87-88 special coordination funds for promoting science and technology]

[Text] **Table of Contents**



### I. Outline of the Research Project

#### 1.1. Objective of the Research

With the competition to develop new materials intensifying among industrially advanced nations, Japan is being pressed to develop new materials on her own, instead of depending on technologies from abroad as she has always done in the past. In particular, demands for materials with higher functions, multiple functions, etc., are growing more pressing in technological domains such as information, electronics, and energy and hope is being pinned on the creation of new materials which are based on a new concept.

Following the successful production of composite materials there has recently emerged a trend of creating new materials—a material with a hybrid structure—which combines various characteristics of metal bond, covalent bond, and ionic bond such that the structure is controlled at the atomic and molecular level in a highly artificial manner and which, hence, may conceivably

yield high functions and multiple functions that surpass those of the present level or that are not predicted on the basis of compounding rule.

It is essential to establish a technology which allows a systematic and thorough application of the structure design based on theories and which is capable of control and analysis assessment of the structure at the atomic and molecular levels if new materials with hybridized structure are to be developed efficiently. The first phase of the research thus involves the following:

(1) Research on the theory for hybridized structure design (2) Research on the database for hybridized structure design (3) Research for development of technologies for control of hybridized structures (4) Research for development of technologies for the analysis and assessment of hybridized structures

In the second phase, results of research on theories, databases, and control of technologies obtained in the first phase for individual materials and for each of the structural dimensions are slated to be integrated into two-component systems of materials—the metal-inorganic material system, the inorganic material-organic material system, and the organic material-metal system—and materials with a hybrid structure involving two components of different material groups and displaying new and high functions are to be created on the basis of the structure-design technology with a view to establishing basic technologies for the development of new materials.

**1.2. Outline of the Research**

**(1) Creation of Hybridized Materials of the Metal-Inorganic Material Type Hybridized materials comprised of a metal and an inorganic material are created by applying relevant theories for structure design, relevant data-bases, and relevant control technologies and a basic technology for developing new materials featured by such properties as superconductivity, electronic-element functions, and dielectric functions is established.**

**1) Research on Superconducting Materials Produced by Lamination**

A laminated film made of a metal and an inorganic material is produced by a multiple target radio frequency sputtering in order to produce a material capable of functioning as a superconducting material at higher temperatures.

**2) Research on Materials Involving Electronic-Element Functions and Produced by Lamination**

The interface between a metal and an inorganic material is controlled at the atomic level by the application of a reactive molecular-beam epitaxy in order to yield a material with high-speed electronic functions.

**3) Research on Materials Involving Electromagnetic Anisotropy and Produced by Lamination**

A laminated film of a metal and an inorganic material is produced by molecular-beam epitaxy, etc. such that electromagnetically anisotropic materials such as a new dielectric are created.

**(2) Creation of Hybridized Materials of the Inorganic Material-Organic Material Type**

Hybridized materials comprised of inorganic and organic materials are created by applying relevant structure-design theories, relevant databases, and relevant control technologies in order to establish basic technologies for developing new materials with properties such as magnetic fluid function, solid electrolyte function, and ion-adsorption function.

**1) Research on Magnetic-Fluid Materials Produced by Application of Fine-Powder Technology**

An inorganic material is finely powdered and turned, with an organic compound, into a composite magnetic fluid of high maximum magnetization.

**2) Research on Solid-Electrolyte Materials by Means of an Ion-Pass-Structure Control Technology**

Using an ion-pass-structure control technology, an organic solid-electrolyte material is paired with an inorganic material such that a material for solid electric cells of the hybrid type with a high electric-current density is created.

**3) Research on Materials Involving Such Properties as Ion Adsorption Conducted by Applying Technologies for Interface-Control Technology Hybridized materials with high performance in such functions as ion-adsorption and catalytic action are created by pairing an organic material with an inorganic material and by controlling interface structure between them.**

**(3) Creation of Hybridized Materials of the Organic Material-Metal Type**

Hybridized materials comprised of an organic material and a metal is created by applying structure design theories, relevant databases, and relevant control technologies in order to establish a basic technology for the development of new materials involving such properties as high electric conductivity and non-linear optical function.

**1) Research on Organic Materials of High Electrical Conductivity To Be Carried Out by Applying Molecular Aggregate (or Microfabrication) Technology**

A laminated film made of an organic material and a metal is prepared by means of organic molecular beam epitaxy such that a material of high electrical conductivity (piezo- and pyro-electric) is created.

**2) Research on Non-Linear-Optical Materials To Be Carried Out by Applying Molecular Orientation Technology**

A laminated film comprised of an organic material and a metal is prepared by molecular orientation technologies for non-linear-optical materials.

**(4) Research on the Function That Helps Development of Ideas for the Creation of Hybridized Materials**

Methods of how to convert the theories, data, and rules systematized for materials of individual groups into those for materials of different groups are studied so that the creation of relevant new materials is facilitated.

**(5) Enhancement of Research**

In order to enhance relevant research projects, evaluations of research results are carried out as are exchanges of information and coordination of work [among researchers] on matters such as research implementation plans and current states of research.

**1.3. Annual Plan for the Research**

| Research Item | Fiscal 1984 | Fiscal 1985 | Fiscal 1986 | Fiscal 1987 | Fiscal 1988 |
|---|---|---|---|---|---|
| 1. Creation of hybrid material of the metal-inorganic material type | | | | second phase | |
| (1) Research on superconducting materials produced by lamination | | | | | |
| (2) Research on materials with electronic-element function produced by lamination | | | | | |
| (3) Research on electromagnetically anisotropic materials produced by lamination | | | | creation of new material | |
| 2. Creation of Hybrid materials of the inorganic material-organic material type | | | | | |
| (1) Research on magnetic-fluid materials produced by fine-powder technology | | | | | |
| (2) Research of solid electrolyte materials produced by ion-pass-structure technology | | | | creation of new material | |
| (3) Research on ion-adsorptive material, etc. by interface-structure technologies | | | | | |
| 3. Creation of hybrid materials of the organic material-metal type | | | | | |
| (1) Research on organic materials of high electrical conductivity using molecular aggregation (microfabrication) technology | | | | | |
| (2) Research on non-linear optical materials using molecular orientation technologies | | | | creation of new material | |
| 4. Research on the function that helps development of ideas for the creation of hybrid materials | | | | development of methods that helps development of ideas | |
| | first phase | | | | |
| Research on theories and data base for hybridized structure design | research on theories and data base | | | | |
| Research on technologies for controlling hybridized structures | development of technologies for controlling structures | | | | |
| Research on technologies for analysis and assessment of hybridized structures | advancement of performance in the measurement system | | | | |
| 5. Enhancement of research | | | | | |
| Required cost (total: in million yen) | 386 | 311 | 174 | 234 | 105 |

### 1.4. Allotment and Costs of Research

| Research Item | Research Organ | Fiscal 1987 | Fiscal 1988 | Total |
|---|---|---|---|---|
| 1. Creation of hybrid materials of the metal-inorganic material type | | 96,826 | 34,448 | 131,274 |
| (1) Research on superconducting materials produced by lamination | National Research Institute for metals of the Science and Technology Agency | 49,309 | 10,929 | 60,238 |
| (2) Research on materials with electronic-device function produced by lamination | Electrotechnical Laboratory of the Industrial Science and Technology Agency, Ministry of International Trade and Industry | 27,365 | 13,842 | 41,207 |
| (3) Research on electromagnetically anisotropic materials produced by lamination | Research and Development Department of the Science and Technology Agency | 20152 | 9677 | 29,829 |
| | Institute for Physical and Chemical Research (commission) | 1,832 | 880 | 2,712 |
| | Tokyo University (recommission) | 18,320 | 8,797 | 27,117 |
| 2. Creation of hybrid materials of the inorganic material-organic material type | | 71,692 | 29,671 | 101,363 |
| (1) Research on magnetic-fluid materials produced by fine-powder technology | National Research Institute for metals of the Science and Technology Agency | 27,093 | 13,978 | 41,071 |
| (2) Research on solid electrolyte materials produced by ion-pass-structure control technology | Research and Development Department of the Science and Technology Agency | 19,214 | 10,256 | 29,470 |
| | Institute for Physical and Chemical Research (commission) | 1,747 | 932 | 2,679 |
| | Osaka University (recommission) | 17,467 | 9,324 | 26,791 |
| (3) Research on materials with ion-adsorptive capacity, etc., using interface-structure control technology | National Institute for Research in Inorganic Materials, Science and Technology Agency | 25,386 | 5,437 | 30,822 |
| 3. Creation of hybridized materials of the inorganic material-metal type | | 59,052 | 37,955 | 97,007 |
| (1) Research on organic materials with high electrical conductivity produced by molecular-aggregated (-micro-fabrication) technology | Research and Development Department of the Science and Technology Agency | | | |
| | Institute for Physical and Chemical Research (commission) | 22,444 | 22,064 | 44,508 |
| (2) Research on materials for non-linear optics produced by molecule-orientation technology | Research Institute for Polymers and Textiles of the Industrial Science and Technology Agency, Ministry of International Trade and Industry | 36,608 | 15,891 | 52,449 |
| 4. Research on the function that helps develop ideas for the creation of hybrids | Research and Development Department of the Science and Technology Agency | | | |
| | Sumitomo Denkou [Electrical Industry] Co., Ltd (commission) | 6,327 | 2,962 | 9,289 |
| 5. Enhancement of research | Research and Development Department of the Science and Technology Agency | 261 | 396 | 657 |
| Total | | 234,158 | 105,432 | 339,590 |

### 1.5. Research Enhancement Committee

| Name | Affiliation |
|---|---|
| Committee chairman | |
| Chouichi Niizeki | Consultant of the department of component materials Toshiba, Co., Ltd. |
| Committee member | |
| Kenichi Ogawa | Director of the department of structure-control research, National Research Institute for Metal, Science and Technology Agency |

| Name | Affiliation |
|---|---|
| Yuzo Katayama | Director of the department of basic-material research, Ibaragi Telecommunications Research Institute, NTT [Co. Ltd.] |
| Masao Kato | Director of the third department of the Research Institute for Polymers and Textiles, Industrial Science and Technology Agency, Ministry of International Trade and Industry |
| Shinichi Shirazaki | General researcher of the first research group, the National Institute for Research in Inorganic Materials, Science and Technology Agency |
| Asao Suzuki | Professor of the Precision-Engineering Laboratories, Tokyo Institute of Technology |
| Masao Doyama | Professor of the Steel Engineering Section of the Engineering Department, Nagoya University |
| Chuu Maekawa | Director of the material department of the Electro-technical Laboratory, Industrial Science and Technology Agency, Ministry of International Trade and Industry |
| Shigezo Murakami | The Board of Directors, Sumitomo Electric Industries Technology Cooperation Co., Ltd. |
| Hiroshi Yamada | Chief Researcher of Riken [Institute of Physical and chemical Research] |

## II. Research Results

### 2.1. Summary

Promoted in the second phase of the present research project is the creation of the three types of hybridized materials comprised of materials of different groups, i.e., those made up of a metal and an inorganic material, an inorganic material and an organic material, and an organic material and a metal. These second-phase research projects represent a collective development of the element technologies for the atomic and molecular level of design, control, function and analysis, assessment of materials which were established by the research on different atoms and molecules of the same group for each metal, inorganic-material, and organic-material groups.

In preparing hybridized materials of the metal-inorganic material type, research on superconductive materials produced by lamination, on materials with electronic-element function produced by lamination, and on materials with electromagnetic anisotropy produced by lamination was encouraged.

In the research on superconductive materials, Pd/Te series were selected for the metal/semiconductor series and BiO/Sr-Ca-Cu-O series for the metal/ceramic series. The former used the molecular-beam epitaxial method (MBE) which successfully allowed control of growth conditions of films with high precision and yielded fine single-phase films of $Pd/Te_2$ ($T_c$: 1.7 K) and Pd/Te ($T_c$; 2,4 K). In the latter, the [layer] period in the direction of c- axis was artificially controlled for high critical-temperature superconductive materials of Bi series by the application of a double-target sputtering method and, consequently, a crystal structure in which four or five layers of Cu-O were sandwiched between two layers of Bi-O was yielded successfully—a structure unobtainable under usual thermal equilibrium.

In the research on materials with electronic-element function produced by lamination, secondly, new metal-semiconductor laminates that allow the electronic element produced from them to function at higher speeds were prepared, their structures assessed, and their electrical properties evaluated. The method of control of the laminate structure used is one that allows a thin metal film to form over a cleaned surface of the semiconductor without involving an interface reaction and one that, in contrast, used positively the interface reaction involved between the metal and the semiconductor. The former method, using the MBE method, allowed a clean surface of GaAs and AlAs to form, the further metal films of Al and Nb and a semiconductor film of GaAs to overlay. In the latter method, an interface reaction of nickel over β-SiC allowed nickel silicide to form by an interface reaction: the growth process of the film and the state of chemical bondings involved were also investigated.

In the research of materials with electromagnetic anisotropy, thirdly, multilayer films of Co/Cu,Mo/Cu, and Ag/Co were produced by radiofrequency sputtering and those of Co/V by MBE with the view of laminating two types of superthin films of different properties alternately and thus to produce a new functional material based on the differences between properties of the film in the interlayer or interlaminar direction and those in the intralayer or transverse direction and an assessment of the films' structures and electromagnetic properties was made.

Creation of hybridized materials of the inorganic material-organic material type which was promoted, involves magnetic-fluid materials produced by fine powder technology, solid electrolyte materials produced by ion-pass-structure control technology, and materials with ion-adsorptive capacity, etc., produced by interface-structure control technology.

First, research on magnetic-fluid materials using a fine powder technology has allowed development of a method for the synthesis of fine particle colloids of metals by subjecting the metal to vacuum-vapor deposition over the surface of an oil involving a surface active agent and, additionally, a method for substitution of the solvents and one for control of the diameter of the particles using thermal treatment and, thus, preparation of metal magnetic fluid of Fe, Co, Ni, and a Fe-Co alloy. Also successfully developed were fine particles of iron

nitride and iron-nitride magnetic fluid by use of a unique plasma CVD. Also a thermal engine using entropy change occurred under a magnetic field was trial-manufactured, and subsequently the kinetic energy was successfully isolated for the first time.

Second, in the research on ion-pass-structure materials, the manner of deposition on a glass plate of a $TiS_2$ film, which is known as having an efficient ion-pass structure and as representing a highly prospective electrode material, was controlled and those films orienting vertically to the substrate in higher ratio were found to have higher discharge capacity and to be capable of incorporating lithium ions with greater ease.

Third, in the research on materials with ion-adsorptive capacity, 24 compounds comprised of a laminar inorganic compound and cyclodextrine were synthesized as hybridized materials of the inorganic material-organic material type. In a typical compound made up of zirconium phosphate and cyclodextrine, in particular, a molecular inclusion capacity was shown to explain the relevant function. Also carried out was research to give higher functions to hybridized materials made up of materials of an identical material group, i.e., those of the inorganic material-inorganic material type, on varistors of ZnO series.

Where creation of hybridized materials of the organic material-metal type is concerned, research on organic materials of high electrical conductivity produced by molecular aggregation (micro-fabrication) technology and on materials of non-linear optics using molecular orientation technology was carried out.

First, in the research on organic materials with high electrical conductivity as produced by molecular aggregation technology using an organic molecular-beam epitaxy (OMBE) apparatus, copper phthalocyanine (CuPc) and milibudenum disulfide ($MoS_2$) single crystals were coupled with use of an organic molecular-beam epitaxy (OMBE) apparatus and subjected to vapor deposition under a superhigh vacuum condition with RHEED in operation, and diffraction picture of the resultant films indicated, as based on the planar arrangement of CuPc over $MoS_2$, that the distance of crystal planes of 13 Angstrom was equivalent to the diameter of the planar molecule CuPc. This was the world's first measurement of the growth of organic molecular films achieved with RHEED. Observation of the resulting film with the scanning tunnel electron spectrum microscope (STS), also proved that the CuPc plane runs parallel with the cleavage plane of the $MoS_2$ crystal in adhesion.

Second, in the research on materials of non-linear optics produced by a molecular orientation technology, hybridized materials with a performance far surpassing that of inorganic dielectrics and the practical currently available materials were developed. Of the poly diacethylene, whose rate in the third-degree nonlinear susceptibility in the nonresonant region which is essential for the high speed response of devices was the largest of all matters available, some samples had their main- and side-chains conjugated with one another (intramolecular hybridization) and their susceptibility went up five times. Several types of poly diacethylenes with prospects for higher performance were further synthesized. The symmetry of the molecular arrangement of the cyanine pigment derivatives was controlled by forming complexes between the compound and an organic ion (intramolecular hybridization) which allowed the value of the practically important d-constant for the resulting crystals to rise higher than those of the presently available materials.

As a result of investigation into the features of the database helping the designing of hybridized materials and into the countermeasures for the areas having shown unsatisfactory research results, research continued and several basic concepts brought out to help develop ideas necessary for creating entirely new and as yet unknown materials.

The present research covering these five years has led to clarifying many questions involved in the creation of new functional materials by means of hybridization of materials having different chemical bondings. Some of the above second-phase results are a milestone for achieving its objectives and also steps for future research.

**2.2. Outline of Results for Individual Research Items**

**1. Creation of Hybridized Materials of the Metal-Inorganic Material Type**

**1.1. Research on Superconductive Materials Produced by Lamination**

The research was conducted with the aim of "improving properties of super-conductive materials by lamination methods" and the research effort was focused on the material types metal/semiconductor and metal/ceramic. The materials actually chosen were thus Pd/Te series for the former and Bi-O/Sr-Ca-Cu-O for the latter. The main aim was to synthesize thin films of laminated structures, which is not possible under ordinary thermal equilibrium. An analysis of the structure and an assessment of superconductivity of the material were also made.

In the Pd/Te series, synthesis of thin films of intermetallic compounds of Pd/Te series and relevant epitaxial growth were performed by means of MBE. The substrate used was the (0001) face of the 2H-$MoS_2$. By controlling with high precision the growth conditions such as molecular-beam intensity and substrate temperature individually, fine single-phase thin films of the intermetallic compound Pd/$Td_2$ were successfully allowed to grow epitaxially with a $T_2$ proved to be 1.7 K. By varying the molecular-beam intensity ratio J(Pd): J(Te) and substrate temperature properly, preparation of the film Pd/Te was also proved possible with a $T_c$ of 2.4 K. In addition the experiment provided a guideline for the possible synthesis of an intermetallic-compound laminate, $PdTe_2$/PdTe.

In the Bi-O/Sr-Ca-Cu-O series of thin films, the structure of superconducting materials of Bi series and of the high-critical-temperature type and, in particular, the period along the c-axis was successfully controlled artificially by means of double-target sputtering. As a consequence, the synthesis of a crystal structure in which four and five layers of Cu-O was sandwiched between two double layers of Bi-O was successfully brought out, a success which provided a new guideline for the artificial synthesis of new superconducting materials.

**1.2. Research on Materials With Electronic-Device Functions Produced by Lamination**

Research was carried on with the view to developing hybrid materials of a hetero-lamination structure including that of metal/semiconductor for high-speed electronic devices, metal/semiconductor with resistance against adverse environmental effect, etc. which allows operation at still higher speeds. That is, laminated structures of the metal/semiconductor type was prepared and assessments of its structure and its electrical properties were conducted.

Two methods of making metal/semiconductor heterostructure materials were tried: One is layer-by-layer lamination of metal thin films over a cleaned surface of a semiconductor with no interface reaction involved, and the other positively utilizes the interface reaction involved in the metal/semiconductor material. In the former, the molecular-beam epitaxy (MBE) allowed formation of a clean surface of a semiconductor of GaAs and AlAs and, subsequently, lamination of metal films of Al and Nb and, that of GaAs semiconductor thin films to give a semiconductor/metal/semiconductor heterostructure. In the latter, an interface reaction of nickel with β-SiC led to the formation of nickel silicide.

For assessment of the growth process of the film, a dynamic assessment technology was developed, using a high-speed electron-beam diffraction method (RHEED) to assess crystallinity, growth process, surface morphology, and surface lattice-strain. Furthermore, the electron spectroscopy and ion scattering methods were used for evaluating the precipitiousness of composition and the states of chemical bondings at the interface.

Where the metal/AlAs, GaAs hetero-lamination structure is concerned, first, epitaxial orientation for the Nb/GaAs lamination was determined and fine quality of the structure for film thickness below 6 nm proved and, second, epitaxial orientation for the lamination structure of Al/AlAs was determined and relevant conditions for the preparation of good structure obtained. The semiconductor/metal/semiconductor structure for GaAs/Al/AlAs was prepared.

In the metal/SiC hetero-lamination structure, metal thin films of Mo, Ni, and Al were grown over β-SiC and the properties of the relevant interface reactions determined. That is, with Mo metal films, the interface-reaction properties varied with different crystal forms. With Ni, conditions for the formation of silicide were determined; with Al, dependence of the interface reactions between Al and Si on its thermal treatment was proved; and preparation of nickel silicide of good quality was made possible.

**1.3. Research on Materials With Electromagnetic Anisotropy Produced by Lamination**

Two types of super-thin films of different properties were laminated alternately with the structure being controlled at the atomic level with a view to developing new functional materials based on the difference between the properties in the interlaminar or interlayer direction and in the transverse/or intralayer direction. Thus, multiple layer films of Co/Cu, Mo/Cu, and Ag/Co were prepared by means of radiofrequency sputtering and those of Cu/Ni and Co/V by MBE. The Co involved in the Co/Cu film was fee in structure and its saturation magnetization tended to fall as lamination cycle progressed. In Mo/Co films, in contrast, Co has a hcp structure and, with a diffusion region existing for several atomic layers at the interface, the film turned paramagnetic as the cycle became short. In Ag/Co, the intensity and the number of the superlattice-reflection peaks was found to grow greater than those in the growing phase when thermal treatments were applied under appropriate conditions. It was also found that the film retained a large residual magnetization in the vertical direction of the film and that its saturation magnetization increases with shorter cycles, exceeding that of the Co bulk. It may make a vertical-magnetization film if further reduction in the thickness of Co layers is possible. In Cu/Ni, it is conceivable that there exists a reduction in ferromagnetic layers for about two layers of nickel atoms at the interface because of mutual diffusion. While the interface of a short cycle multiple layered film is aligned, it undergoes a transition from alignment to non-alignment at a longer cycle of 49 Angstrom and then the electrical resistance changes abruptly. In V/Co, the value of specific heat is reciprocally proportional to that of longer periods but shifts upward from that straight line for shorter-period regions. Measurements of thermal diffusion rate by optical alternating current process has proved that the dependence on the period of electrical conductivity is larger than that of thermal conductivity.

**2. Creation of Hybridized Materials of the Inorganic Material-Organic Material Type**

**2.1. Research on Magnetic-Fluid Materials Produced by Fine-Powder Technology**

Fine particles with an extremely small particle diameter mostly exhibit unique properties which are absent in bulk materials having ordinary particle size. It is not easy to determine the property that very fine metal particles inherently carry because the particles are subject to oxidation and to aggregation into large clusters. This has been a snag in the progress of basic research on the property of very fine particles as well as in their application in new materials.

The present research has led to development of a unique vacuum vapor deposition method in which metals are subjected to vacuum vapor deposition over a surface of oil containing a wetting agent. The ferromagnetic metal particulates (each particle measures about 2mm in diameter) are coated with wetting agent molecules, therefore the high concentration colloid metal synthesized at this time is free from surface oxidation and dispersed evenly without coagulating fine particulates. These metal colloids are subjected to such advanced measurement methods as those of micro-beam electron-beam diffraction, Mossbauer effects, and microwave magnetic resonance. Such problems as crystalline structures unique to fine particles, abnormality of atomic magnetic moment, and dynamic magnetization of fine particles are experimentally shown.

In addition to the synthetic technology for fine metal colloid by the vacuum vapor deposition, substitution of solvents and control of particle diameters using thermal treatment were developed in this research as were metal magnetic fluid of iron, cobalt, nickel, and iron-cobalt alloys: a unique plasma CVD method, fine particles of iron nitride, and a magnetic fluid of iron nitride, were developed. A trial manufacture of a magnetic-fluid thermal engine based on the entropy change occurred when the magnetic fluid was under magnetic field—an example of the application of magnetic fluids—was first successfully carried out and the kinetic energy was successfully isolated. A series of patents granted during this research are presently being used by ten-odd companies, thereby projects for practical application of magnetic fluids of high performance are being promoted.

### 2.2. Research on Solid-Electrolyte Materials Produced by Ion-Pass-Structure Control Technologies

If materials with effective ion-pass structure are to be used as a solid state battery, it is necessary to control crystal face such that easy flow of ions into and out of the electrode is allowed and hence a large current density is made available. In the research presented here, a $TiS_2$ film which is called a prospective material for electrodes because of its structural anisotropy was prepared with its deposition mode under control and an efficient electrode material produced.

The manner in which the fine-crystal thin film of $TiS_2$ deposits on a glass substrate was controlled by varying relevant conditions for thin-film formation, e.g., the composition of the material gas for plasma CVD of $H_2S$ and $TiCl_2$, the purity of the gas, the flow rate, the substrate temperature, and applied plasma output. The result proved that a $TiS_2$ layer oriented in parallel with the substrate when the rate of deposition was low. When the rate is high, the c face of the hexagonal system was deposited parallel to the substrate in the early phase of deposition while, as the film thickness increases, the c face changed to vertical orientation, which is conceivably favorable for electrode materials. Preparation of films of different thickness with the deposition rate fixed also proved that the $TiS_2$ layer runs parallel to the substrate when the film was thin, but that the layer was made to run vertical to the substrate as its thickness increased beyond 10μm because of a change taking place in the priority orientation of deposition. Preparation of $TiS_2$-Li cells incorporating these films then proved that the greater the proportion of the $TiS_2$ film orienting vertically to the substrate, the greater was the discharge capacity of the cell and easier was the intake of lithium ions.

### 2.3. Research on Materials With Ion-Adsorptive Capacity and Other Features Produced by Interface-Structure Control Technologies

This research is aimed at development, on the basis of a material design scheme, of hybridized materials with such functions as ion adsorption/exchange, catalytic actions, piezoelectric actions, and semiconductor capacity. The content to the research falls largely under two groups: One involves creation of hybridized materials of the inorganic material-organic material type which is made up of two different material groups and the other of hybridized materials of high performance made up of two same type inorganic materials.

In the first group, new compounds were derived from compounds of the inorganic material-organic material type made up of a laminar inorganic compound (zirconium phosphate or monmolilonite) and cyclodextrin which was successfully synthesized in the phase I of the present research. The compounds so obtained in both phases I and II totaled 24. The structure and mechanism of hybridization for these compounds were determined as were general rules of hybridization. In addition, the capacity for inclusion of molecules was demonstrated for the typical compound constituted by zirconium phosphate and cyclodextrin and the mechanism involved elucidated.

In the next research, varistors of ZnO series were taken as the representative example of hybridized materials of the identical-material-group type, and the structure and composition of their three-phase grain boundary were determined as were their electrical properties. Also reported was the fact that the deterioration of the varistor by reducing atmospheric species involved changes in the grain-boundary structure produced by transfer of oxygen through the three-phase grain boundary.

## 3. Creation of Hybridized Materials of the Organic Material-Metal Type

### 3.1. Research on Organic Materials of High Electrical Conductivity Produced by Molecular Aggregation (Micro-Fabrication) Technologies

In pursuit of either new properties materialized in super-thin organic films sandwiched between a material of a different group or optical and electronic functions exhibited in laminates of this super-thin film, an apparatus for an organic molecular-beam epitaxy (OMBE) was designed for hybridization technology and particularly

for dealing with organic matter. As a result of trial and error to improve the apparatus and select the organic compound and inorganic metal substrate, a coupling of copper phthalo-cyanine (CuPc) with a cleaved surface of the single crystal milibudenum disulfide was adopted and the materials subjected to vapor deposition in a superhigh vacuum of $10^{-9}$ - $10^{-10}$ with RHEED in operation. The one-molecular-layer thickness of materials so obtained were observed by STS (scan type tunnel electron spectrum microscope) in real space.

The RHEED afforded a clear picture of diffraction streak based on a planar coordination of CuPc over $MoS_2$ and displayed a crystal interval of 13 Angstrom which was equivalent to the diameter of the planar molecule of CuPc. This exploration was the first achieved in the world in pursuit of organic molecules with RHEED. The STS picture demonstrated that the CuPc molecule runs parallel with the cleaved face of the single crystal $MoS_2$ in adhesion. Since Van der Vaals-London interaction largely dictated between the molecules $MoS_2$ and CuPc, it was concluded that a lattice-nonmatching epitaxial growth prevailed in the composite formation.

Above results provided a guideline for selection of organic group of compounds and inorganic group of materials and suggested the possibility that these composites in the superlattice state make type II superconductor.

**3.2. Research on the Nonlinear Optical Materials Produced by Molecular Orientation Technologies**

Hybrid materials for nonlinear optics that is far superior in performance to the presently available materials derived from inorganic dielectric materials have been developed on the basis of the superorientation structure control technology established in the phase I research for organic materials.

First, in connection with the conjugated polymer poly diacethylene that, of all the materials ever available, exhibited the maximum value in the tertially or cubic nonlinear sensitivity in the nonresonance region—a property which is indispensable in high speed response—methods for designing and synthesis of solid phase polymerization that provides the molecule a structure of conjugation between the main and the side chains (intramolecular hybridization) were developed and expanded, with some samples exhibiting a rise in sensitivity value some five times larger and the correctness of the methodology thereby being proved. In parallel with this, several poli diacethylenes with a good prospect of higher functioning were also synthesized. Second, in the case of cyanine pigments, these involved difficulties in crystallizing the secondary activity in spite of the excellent nonlinear optical properties of the very molecule. The crystal of the molecule afforded a value for the very important d constant which exceeded that for 2-methyl 5-nitro aniline, the highest so far known and which was 400 times that of the practically available $KH_2PO_4$ when it was coupled with organic ions for complex formation (intermolecular hybridization), thereby having their symmetry of molecular arrangement controlled. Third, regarding the polar-structure architecture method wherein two different mono- (or single-molecular-layer) molecular films are laminated alternately (intermolecular hybridization) to give super-thin films of secondary activity, addition of a mono-molecular films of an amorphous polymer for the formation of a superlattice was investigated. It was consequently found that this method prevented the film from turning translucent, a disadvantage which results from development of domains, which posed the biggest problem, in the optical application of polar-structure laminate films made up exclusively of crystalline mono-molecular films. The method thereby proved to have the prospect of allowing a powerful means for preparing transparent films that involve polarity in spite of their amorphous glassy state without applying the polling procedure required in the past methods.

In the metal hybridized materials, orientation-controlled vapor-deposition conditions were estimated in terms of molecular structures, kinds of substrates, temperature, etc. for pigments and poly diacethylenes, followed by preparation of materials for thin-film bonding. Though an increase in the development of harmonics was noted from an assessment of the nonlinear optical properties by the ATR method, it is not yet known whether or not an improvement in properties resulting form hybrid interaction took place except for an increase in the intensity of signals due to surface plasmons transmitted through wave-guide.

**4. Research on Functions Assisting Development of Ideas for the Creation of Hybrid Materials**

**1. Examination of the Features of the Conventional Database and of the Area Yielding Unsatisfactory Results and Relevant Countermeasures**

(1) The database (including knowledge system) is effective as a basic technology in the research on material development and many results have been achieved in structure design, quality prediction, experiment simulation, etc. Theoretically, this is a deductive inference support type function.

(2) In research in the phase of exploration for new and unknown domains, data and guiding principles available are limited, strong and precise deduction is difficult to obtain, and hence a new kind of database is in demand. One method available here as a inducive inference support type and is referred to as the "idea-development and discovery support type (CAIF)" in this article where creation of system concepts is tried and Ver. I. is proposed.

**2. Outline of the "CAIF" [Computer Assisted Idea Formation]**

(1) "Concepts units and their architecture", "emphasis on associative stimulus," "information interaction process" etc. were defined as the basis.

(2) As an instrument for promoting ideas, "word frame (characterized concept units)" which computer graphics, "associative pattern display" and "recording of thought development" were created using the computer graphics "word frame (characterized concept units)" and "connectors." These are called "Associated Database" made of a combination of data, information, and knowledge.

(3) New viewpoints such as "LIVEWARE approach", "W-H association (oriented association stimulus)" "structure-oriented (structurism) database" were created and are presently being scrutinized.

**III. Extended Effects of the Research and Problems Involved Therein**

**3.1. Significance of the Research and Its Extended Effects**

**3.1.1. Creation of Hybrid Materials of the Metal-Inorganic Material Type**

In the research on the hybridized materials of the metal-inorganic material (semiconductor, ceramic) type, the objective was to establish technologies for laminating materials of different groups together, assess the synthesized laminate films and measure relevant physical properties. Superconductivity, functional properties of electronic elements, and electro-magnetic anisotropy were selected for investigation.

Whereas materials of different material groups generally exhibit different modes of bonding and lamination of these different groups of materials together itself is hard, the interface, if produced at all, has the prospect of displaying properties which are not expected in common laminates made up of a single phase or of materials of an identical material group. Representative cases of this phenomenon which has already been demonstrated includes GaAs related HEMT (high electron mobility transistor) and high-temperature oxide type of superconductivity materials.

Of significance in the research on superconductive materials was the demonstration of the synthesis of thin films of the intermetallic compound $PdTe_2/PdTe$, suggesting the possibility of its application in laminates. Since intermetallic compounds are comprised of a wide range of materials involving metals, ionic crystals, and semiconductors, this was a breakthrough in the research on lamination of materials of different material groups together. The experiments also have demonstrated that the number of the crystal faces of the $CuO_2$ of an oxide superconductor was controllable, which implies that improvement of superconducting properties of an oxide superconductor is possible as are the artificial synthesis of new materials, the extended effects of which is beyond calculation.

In the case of research on materials with functions of electronic elements produced by lamination, creating the conditions for preparing films of the intermetallic compound GaAs/Al/AlAs is significant in that various projected devices of compounds involving an element of the III - V groups have advanced a step further toward materialization. The research on the lamination structure of composites, metal/SiC has proved that its physical properties are heavily dependent on the crystalline structure of the silicide. The research thus yielded a guideline for designing a hetero-lamination structure, metal/environment-resistant semiconductor.

In the research on electro-magnetically anisotropic materials, multiple laminated films of Co/Cu, Mo/Co, Ag/Co, Cu/Ni, and Co/V were produced. Films of Ag/Co series showed major residual magnetization in the vertical direction. Its saturation magnetization increased with decreasing period of lamination until it exceeded that of Co in bulk. There seems to be a good prospect for making a vertical magnetized film, provided the condition for preparing it is optimized.

**3.1.2. Creation of Hybrid Materials of the Inorganic Material-Organic Material Type**

Hybrid materials may be defined as materials in which new functions or functions whose level exceeds conventional ones are achieved by means of compositing structures, microstructures, bonding modes, etc., in a sophisticated manner.

One type of hybrid material is made from materials of an identical group, and the other from materials of different groups, with both involving sophisticated composition. In the first phase of the present research project, research subjects were chosen regardless of whether the hybrid material was made from materials of an identical material group or from different material groups. In the second phase, hybrid materials made from materials of different material groups were the subject for the most part, and those made from materials of the same material group studied only as a supplement.

Major themes includes magnetic materials as a sophisticated composite made up of an organic medium and superfine metal particles and materials with ion-adsorptive capacity wherein cyclodextrin or one of its derivatives is subjected to inclusion into a laminar structure such as those of montmorillonite or zirconium phosphate. Also studied were: the electrode material for solid electrolyte battery, $TiS_2$, of laminar structure and grain-boundary application materials such as varistor and posistor which represents a sophisticated composite-formation of the grain boundary (insulation phase) and the hose (electro-conductive phase). At the start of the second phase research, attention was primarily given to research on hybrids whose materials are from different materials groups. The actual research target tended to be

the extension of the line of the first phase research, which seems to have contributed largely to the good research achievements.

Regarding research on magnetic fluid, the leading topic in the present hybrid-material type, iron and cobalt magnetic fluids of high functions were prepared on the basis of the activated-interface vapor-deposition method developed in the first-phase research and the behavior unique to very fine particles was thus detected, with relevant analysis then carried out. It was particularly notable that fine iron particles showed higher magnetization than its bulk did. Understanding of this phenomenon may possible have a profound effect on the field of magnetics.

In the research on $TiS_2$ electrode films, the required condition is that the direction of the lamination be normal to the plane of the solid electrolyte, a goal that has been nearly been attained. The technology involved may possibly yield a clue to the technologies for control of the orientation of films.

While a technology for inclusion of cyclodextrin into zirconium phosphate and montmorrilonite was established in the first phase, derivatives of cyclodextrin were successfully subjected to inclusion in the second phase, thereby triggering a new area in the host-guest science, a global theme.

Determining the grain-boundary structure represents one of the major targets regarding ceramic materials. Though varistors and posistors are regarded as a typical hybrid material comprised of the grain-boundary insulation phase and the host insulation phase, the mechanism of formation of its grain-boundary potential barrier has yet to be determined. Under the circumstances, the grain boundary has recently proved to exist under severe oxygen deficiency which was contrary to general expectations and its effect on the varistor characteristics has been studied. In addition, a new concept has been suggested for the mechanism of semiconductorization, which may possibly be considered basic in the material sciences.

### 3.1.3. Creation of Hybrid Materials of the Organic Material-Metal Type

There are many views on research and development of hybrid materials depending on the context. Generally a material is given its name not just upon its emergence but after its application and methods of industrialization have been established, as was proved in composites (composite materials). Hybrid materials began with a concept which preceded the actual material which was destined to exist in the next generation, and represented a new material which was to emerge during the historical process in which a composite material was developed from the three monolithic materials. Research on hybrid materials might lead to hybrid materials as some people insist. Nevertheless, transition from macro- to microstructure such as converting powder into much finer particles, fibers into very thin filaments, and films into very thin films encounters technological difficulties at the micron or submicron level preventing control of the microstructure at the nanometer level. It is here that formation of the microstructure by aggregation of atoms and molecules becomes necessary. Materials turned into solids by aggregation of atoms and molecules are called hybrids: hybridization of a material is based on the technologies for aggregation of atoms and molecules or microfabrication.

Scientific knowledge on the field of "hybrid materials of the organic material-metal type," the subject of this section, is almost nil. Many agents were developed long ago in the fields of organic and polymer chemistry for rust prevention and bonding, but there seems to be a long way to go before reaching the goal because the basic science regarding surface and interface is poor. With recent general use of the apparatus STM that allows direct observation of surfaces, a quick advance is expected, in this research area—hybridization of materials of the organic material-metal type—because it runs parallel to rapid development of basic science regarding surface and interface.

Formation of interface at an atomic level between an organic material and a metal is most difficult compared to other two combinations of material groups. That's because the common temperature range for chemical bonding is narrower for the interface between an organic material and a metal in addition to the small interaction of the molecules. For rust prevention and adhesion, invisible metal oxide layers of the metal surface layers are bonded. With this in mind, the organic/metal hybrid materials development must be based on the scientific knowledge obtained for the organic/inorganic hybrid materials development.

The term 'hybrid material' was first suggested in the present research project based on STA's fund to promote science and technology; in another research either at home or abroad is the same term hybrid used. Regardless of whether the term 'hybrid material' is used or not, the research trend to create new material states by controlling aggregation of atoms and molecules is growing greater and greater in various fields, to which the STA fund must ahve contributed substantially.

Seven years ago, the French government organ CNRS invited the author to visit soon after he suggested the term 'hybrid material.' Immediately after, the organ established interdisciplinary sections and the activities of them—called Electro-active Materials—were enhanced jointly by industrial and academic circles. Whether they did not totally understand the philosophy and concept of 'hybrid' or they chose the term 'electro-active' instead of 'hybrid' because of the absence of the latter term in the French vocabulary, researchers of the CNRS shifted the direction of their research toward practical science. There seems to be one or two projects overseas to establish laboratories with the term "hybrid materials" as part of their name. It is heartening to see

that hybrid material laboratories are being established among private corporations in Japan.

One extended result may be quoted from an investigation based on a science research subsidy "General Investigation and Research on the Emergence of New Functional Materials and the Basis of Their Design" (Prof. Teiji Tsuruta) which was conducted in 1984, the year the present project based on the coordination fund also started. The report, focusing attention of creating materials at the atomic and molecular level and relevant hybridization, was worked out by March 1985. This must be a result of the "Report on Investigation Into Research Project Designs of Hybrid Materials" (I. September 1982; II. February 1983; Research Institute for Physics and Chemistry; Hybrid Material Committee; National Institute for Research in Inorganic Materials; National Research Institute for Metal). A lecture meeting was also held by the 5th section of the Science Council of Japan in February 1985 and differences between the hybrid materials other boundary region materials were discussed. The November 1983 issue of "KOGYOO ZAIRYOO " published by Nikkan Kogyoo Shinbun-Sha", carried feature articles, "Hybrid Materials Unfurled" and since then numerous science and technology journals have published related reports.

### 3.1.4. Research on the Function That Helps Development of Ideas for the Creation of Hybrid Materials

(1) By proposing the centralized process for data for different groups of materials, "other ideas with knowledge of different fields" can be effectively promoted.

The true nature of hybridization of materials resides in combining materials of different material groups and allowing their interaction at the electronic level to proceed such that new properties which single material can not be developed. It is therefore essential that data, information, and knowledge of materials of different material groups, e.g., those of the metal group and the organic material group, be scrutinized from all [chemical and physical] points of view.

A conventional database allows data processing only when interaction is excellent so that actual association diagram can be drawn.

As a matter of fact, correlations of various parameters among materials of an identical material group are used, but those among materials of different material groups are not accessible because of differences in measurement methods.

Present concept, in contrast, does not present the association as a prerequisite, but rather hypothesis for development of ideas and discovery.

In other words, the conventional database is deduction support while the present new concept is induction support, therefore its effect cannot be estimated in value. However, currently there is almost no relational data processing method available, so the new concept is considered to have a pioneering effect on knowledge combination support method for different groups or fields.

It also seems necessary, in spite of the above, to subject the present draft proposition, where many contradictions remain, to further reviews and corrections on the basis that conventional deduction support databases have been gradually refined by research and practical application.

(2) Concepts seem to result in creating technological and substantive needs.

It is said that ideas and concepts underlie the development of science and technology. As mentioned in another chapter, in this discussion also, the method of forming ideas was set up first as the base and the system image was created on top of it. It may be compared to story telling, but differs from simple science fiction in that the author is confident in the substantive nature of the technological seeds [available information] and needs [commercial demands]. This confidence in technological development must be traded off with the advancing nature of the technology in a sophisticated balance, but the author will concentrate here on the main character of concepts and quote some examples of their extended effects.

(i) "Producing and changing mutual correlations of thinking" may best be achieved by applying supercomputers, particularly the parallel type, because additions and corrections of correlations lead to changes of index of each thinking and to a large amount of vector calculations. The high-speed calculation of the supercomputer has displayed its advantages in processing numerical values, but the present research project must be the first to utilize it in dealing with databases and information systems.

(ii) In order to develop "wide-range viewing and focus control display," a visual technique using multiple projectors in addition to the conventional CRT display method is preferable. It may be a better means than paper and pencil if it becomes capable of providing an immediate view of about ten sheets of a notebook at a stretch.

The function helping the intellectual productive activity based on the associative stimulus using the "associated database" which is suggested in the present research project and which represents associations of data or idea units may well depend on the materialization of this kind of technique.

Several research works in MiT's Media Lab are very supportive of this.

(iii) A new concept, "impression(ist)-like information system (database), involves attempts to allow human feeling to emerge in relevant creative activities as it

allows human reason to do. Since the electronic computer may have developed from a calculator to a computer and further to a data processor in terms of function, the concept suggests aiming at an impression(ist) processor as its advanced course.

Materialization of this kind of machine involves various technological requirement. In terms of their output and input power, for example, the speed of the machine must be greater than the conventional machines by an order of magnitude of $10^4$ - $10^5$. In contrast, it may also involve, in the authors' view, a front-end processor utilizing the color tone, fuzzy and dynamic (animation) characteristics.

(iv) A new concept. "Structual(ism) knowledge system (database)", requires a new architecture and a new language. The system does not describe a truth (a new correlation to be subjected to new ideas, a new rule to be discovered, etc.) in a decisive and positive way in order to effectively help relevant induction, but appeals to the human mind in a non-central manner with categorical imagery. It does not mean to deal with data in a conventional manner but to allow something yet unknown in detail to emerge on the basis of "a group of associated data (idea units)" created by thinking activities of individuals (a kind of personal thesaurus, equivalent to "associated type of database"). The author here suggests grasping the truth as "structure" and the associated type of database as the "surface layer"; "structural(ism)," is a related concept and has an assigned architecture which may possibly have projection and conversion at its base.

(3) The objective of this research is to create a new database and, with intellectual activities as the subject of research, various helping tools and functions have branched out as the extended effects, which include "communication tools of high context", "thought-development recording (brain storming conference records)", "thought process recording" and "association enhancement of the problem solving or orienting type". These may all be regarded as variations from the basic rule of expression by idea units, and their associations as pattern representations and their optimal finishes make the key issue for the future.

### 3.2. Present State and Future Prospect of Contribution to Society and the Economy of Hybrid Materials

#### 3.2.1. Creation of Hybrid Materials of the Metal-Inorganic Material Type

The significance of the present research project for having demonstrated structures of hybrids of the metal-inorganic material type is enormous although at present the research is still in its very early, basic phase. As described below, the significance of having demonstrated the possibility of the preparation of hybridized materials of the metal-inorganic material type is pronounced since the combination of materials between those of different material groups is innumerable and thus the possibility of harboring some materials with a required function is high.

Demonstration of the preparation of laminate films for intermetallic compounds is of significance since the compounds are comprised of multiple material groups, i.e., ion crystals, semiconductors, and metals. It opened the way toward materialization of hybridized materials of different material groups.

The fact that lamination of Bi-O double layer/Sr-Ca-Cu-O was successfully accomplished on the basis of hybridization and that the number of Cu-O atom layers sandwiched between two Bi-O double layers was rendered controllable is also very notable because the laminate has the prospect of playing a major roll in the synthesis of new superconductive material of the high-temperature oxide type.

Successful demonstration of the GaAs/Al/AlAs structure is another factor contributing to the bright future of this research field. It clarified the functional properties of the metal/semiconductor interface and also opened the way toward applicaiton in electronic devices.

The non-solid solution type of Ag/Co series, which gave a clue to the preparation of vertically magnetized films also has good prospects. In the non-solid-solution type of hybrids, no diffusion layers exist at the laminate interface in principle. Much is expected regarding improved vertical magnetization characteristics by optimizing laminating conditions and this will open the way toward success in high-density magnetic recording.

The successful hybridization of materials between materials of different material groups thus is the main first step in major advances in superconductivity, electrical properties, and magnetic properties.

#### 3.2.2. Creation of Hybrid Materials of the Inorganic Material-Organic Material Type

Numerous patents have been granted for magnetic fluids, a hybridized material of the fine metal powder/organic medium type. Several corporations, noting the excellent properties of the materials, are working together in the project. There is a new technology for preparing the fiber $TiB_2$, research on which runs parallel with the above, which seems to have good prospects as a prospective material for fiber reinforcement.

A series of inclusion materials which were discovered for zirconium phosphate or montmorrilonite coupled with one of the cyclodextrins are being assessed for their values through a wide range of tests for catalytic characteristics and for micro-capsules.

The critical issue in the practical application of the solid electrolyte $\beta$-$Al_2O_3$—the prospective material for the battery of an electric automobile—resides in the battery electrodes. Under this condition, the technology for orienting $TiS_2$ films for the electrode has nearly been accomplished with values for discharge characteristics

and utilization rate having surpassed those for conventional materials. This is considered an advance toward practical application of the solid electrolyte.

Finally, in connection with varistors and posistors of which the materials are produced by grain-boundary applicaiton, a high-quality posistor with a rise in performance of the order of magnitude of $10^8$ was developed on the basis of a material design plan derived from the mechanism of formation of the potential barrier suggested, as was a varistor with a performance index $\alpha$ being independent of the sintering temperature and one with the value being satisfactory without the addition of $Bi_2O_3$.

### 3.2.3. Creation of Hybrid Materials of the Organic Material-Metal Type

In general, materials industries go downstream from the raw material, to the material, to the processing industry, and finally to the fabricated-product industry. The industry scale grows as the industry goes downstream. The profit gained is very small for the upstream industry and increases going downstream with the ratio being around 1 : 3 : 6. Hybridization of materials implies creation of new materials and hence contributes directly to the raw material industry. Though the needs for raw materials go upstream and a new material thus produced exerts its effects again downstream, it is only the raw material industry that bears the burden of developing and creating the material. The present trend for reorganizing industries within the entire economy and for cooperation among organic material-, inorganic material- and metal-industries, as suggested by the Materials Federation Forum will be promoted in the 5th cycle of industrial activity and prosperity, which has just recently begun, thereby contributing in large measure to industries of information and communications, aerospace projects, energy, and life sciences, with the possibility of sufficiently high results.

Many learned men believe that physics and chemistry will merge (or be hybridized) in the future. The concept of hybrid materials is undoubtedly based on chemical physics and physical chemistry. Hybridization technology comes from the inherent continuity of all sciences and technologies. The history of development of the material sciences and technology suggests that science and technology will inevitably find its future activity in interdisciplinary fields. If the high-value-added materials of interdisciplinary fields represent the future, the term hybrid material might be more appropriate than composite material.

The present society desires the emergency of superfunctional materials over highly functional materials, that is, it seeks to imbue artificially produced materials with life functions. This is manifested, for example, in intelligent materials. In reality, materialization is still a long way off. The policy adopted by the administration is to promote research on second and third hybrid materials. Other nations still remain unaware of the possible material formation at the atomic and molecular level. If the wisdom of the people is concentrated for the successful creation of a raw material of this type and its subsequent commercialization, problems such as trade imbalance, technology-friction, and ownership of intellectual properties which overseas nations are pressing Japan to solve will vanish. industrially advanced nations and particularly those with scarce natural resources like Japan seems to turn into an information-oriented society. A nation's security, on the other hand, is said to reside in productive activity. Japan, with macroscopic production becoming impossible and multi-type small-quantity production being adopted, must inevitably choose production of high-value-added merchandise on a small scale with high grade technologies. Here the Japanese must note that hybrid materials and this concept determines innovations of the nation's production industry.

### 3.2.4. Research on the Functions Helping Development of Ideas for the Creation of Hybrid Materials

**(1) Helping and enhancing research to create materials that belong to a new category.**

This research subject started with working out a measure which is required for producing a so-called database by coordinating organically and systematically data (information) in combination with theory (information - knowledge) as a basic technology for creating new materials. Though the objective was attained in the first phase of the research project, it was proved in the process of the research that there exists a potential requirement which the conventional database technologies can not afford to deal with, name, apart from those cases where efficiency in material development is enhanced by inference made by the applicaiton of theory (knowledge) and data conventionally available, there exists challenging research involving an entirely new concept such as hybrid materials where theories and data are scarce and where even affording vague orientation for the research, simply predicting or guessing can become good subject for research.

Dealing with such cases with the conventional type of database will lead the researcher to contradiction because the database allows enhancement of research efficiency only in conventional terms. However, the desire to raise the efficiency or the degree of achievement of an experiment by using any aid to intellectual activity is more intense in such areas of unexplored new materials. In the event a database or a knowledge syustem involving "functions helping development of ideas"—a concept suggested in the present research project—is made commercially available, it makes a basic technology in creating guiding principles for development of new materials and thus has the effect of enhancing development of new materials.

Helping development of new materials on the basis of the conventional rules is of course important in terms of the possibility of its contribution to society and the

economy, but creation of new materials involving creation of new rules on which to base creation of the material may possibly have greater impact on the infrastructure of society and the economy for the very reason that it is not anticipated. A database or a knowledge syustem as represented by the above concept, therefore, may possibly greatly contribute to society and the economy.

**(2) Prospect of making a new breakthrough in database research**

Database research seem to be marking time presently and this may reflect the fact that conventional research has fully blossomed, entered into the stage of practical application, and is presently dealing largely with application research and very sophisticated advanced applications. The present research project, in contrast, is going to tackle the problem again from the formation of very basic-concepts. When classified in terms of the significance of database research, the researchers in conventional research seem to be engaged largely in research of deduction-inference type knowledge systems and particularly those using correlation type databases.

The present research project belongs in the area of induction-inference rather than deduction-inference since it is in the exploratory stage in an unexplored area. The research thus has to confront a knowledge system (database) of the induction-inference type which is still unadvanced because of the difficulties involved. Namely, it was an attempt to create a general rule from the chaos of a group of unsystematized uncoordinated individual cases (symbolized by data, information, knowledge, etc.) and to make a breakthrough in database research of a new orientation where new ideas, new viewpoints, new discoveries and other creative actions are given priority.

With the main theme of the CODATA world convention for 1990 to be "Data for Discovery", the world trend is gradually moving toward induction-inference support and intuition support. The author was invited to the same convention in 1988 and delivered a lecture during which the exploratory nature of the present research seemed to be recognized by the audience.

The present database research largely concerns the correlation type which originated in the West and which seems to be supported and used by many Japanese researchers. Where the database of the induction-inference type is concerned, research in Japan seems to keep up with that of the West and, in particular, the approach by an induction inference and intuition support which may be more oriented to Oriental than to Western thought is drawing attention of researchers in the West. A breakthrough made in this orientation may most probably contribute greatly to the international community.

**(3) Large potential market of the induction-inference type database**

Research methods may be represented symbolically by the terms "Decartes-like" and "Edison-like". The conventional database is represented by the former, whereas the new concepts involved in the present research project is aimed at creating tools for the latter. Since the two methods complement each other like the two wheels of a cart, the new market for the latter database has the prospect of being no smaller in scale.

**(4) The new database will be a new form for representing intellectual ownership rights and create a stimulus for enhancing intellectual productivity.**

The present system of concepts organizes the "associated type of database" by associating unsystematized data by thoughts and ideas of individual. The resulting database must be protected by a copyright and has the prospect of enhancing intellectual productivity by a computer-aided operation.

Help for original and pioneering research is globally desired. Court trials for patent rights and intellectual ownership are growing more intensive in recent years. A technique to present ideas, concepts, and planning quickly is keenly desired.

### 3.3. Future Problems

#### 3.3.1. Creation of Hybrid Materials of the Metal-Inorganic Material Type

As for hybrids of the metal-inorganic material type, lamination of materials involving different modes of bonding has been handled, but basic knowledge such as the manner in which they are bonded together at the interface is almost nil. In the case of Mo/SiC, a good Schootky barrier was produced when SiC crystal structure was 6H/SiC, but it was not when the structure was 3C-SiC where mere ohmic characters were shown. The relationship between crystal forms and interface characteristics remains to be resolved as one of the research targets.

Another technological question in terms of preparing material specimens which arose when a ceramic, and particularly an oxide, was chosen as an inorganic material was how to introduce oxygen to the material. At present, oxidation is carried out by providing a covering or a hood closely surrounding the substrate holder and thus by raising oxygen pressure in the vicinity of the substrate. The idea for this technique came from the existing sputtering and vapor deposition apparatuses, but it may be necessasry in the future to design an apparatus to which oxygen together with others are introduced from the beginning and which is available for a new method for thin film synthesis such as CVD.

The problems such as lattice irregularity, difference in thermal expansion coefficient, and diffusion layer at the interface that confronted hybrids comprised of materials of an identical material group also cannot be ignored in

hybrids made up of materials of different material groups. It has been demonstrated that the solution of the problem of diffusion is in principle possible by using a phase-equilibrium intermetallic compound (e.g., PdTe - $PdTe_2$), or by selecting non-solid solution group (e.g., A/Co).

The functional properties of hybrid laminates of the metal-inorganic material type have not been subjected to thorough research in these two years, but fortunately signs have emerged for the good prospect that some of these materials must find applications by virtue of their superconductivity, electrical properties at the interface, magnetic properties, etc.

### 3.3.2. Creation of Hybrid Materials of the Inorganic Material-Organic Material Type

An academic question to be solved for magnetic fluids is the reason why high magnetization is seen in very fine particles. The solution may possibly greatly contribute in the meso-stage science. Where their applications are concerned, it seems that private corporations push ahead with improving their function and lowering costs by establishing control technology for the activated interface vapor deposition method.

Where the cyclodextrin montmorrilonite-CD [cyclodextrine] syustem of inclusion materials is concerned, time will tell whether the hybrid system is made commercially available as catalysts and microcapsules. A thorough investigation of the hybrid by allowing transfer of relevant technologies to private concerns is necessary. Same can be said for $TiS_2$ which is the electrode for the solid electrolyte battery.

The new mechanism of semiconductorization involving the host of grain-boundary materials stands in contrast to the conventional mechanism involving control of valences. At present this is a global question for which an early solution is sought. It is also hoped that a comprehensive investigation be carried out and relevant technologies be established for the varistor and posistor of high performance developed by the present research.

### 3.3.3. Creation of Hybrid Materials of the Organic Material-Metal Type

Research on materials of this hybrid type, as seen in the research results described below has just taken its first step. As for the OMBE apparatus, in particular, with no precedence available for its manufacture, time seems to have been lost in trial and error in its trial manufacture. The apparatus for OMBE, like that for MBE, takes time in vapor deposition and thus creates an obstacle in faster research. With combinations of materials of the organic materials-metal type and of the organic material-inorganic material type being available in unlimited numbers, future experiments may need apparatuses which allow simultaneous vapor deposition of numerous specimens of simplified small-scale ones operated in parallel.

The OMBE technology is not necessarily an exclusive one for vacuum hybridization. Faster processing may be made possible under a vacuum of lesser intensity providing relevant organic compounds are selected properly. The wet type of hybridization technologies such as LB also must be converted such that the organic material and the metal be allowed to make contact directly. The STM assessment has brought out a possibility of new development for the preparation of super-thin films made by adsorption, on the surface of solids, of molecules in the liquid state.

Of the hybrid materials of the organic materials-metal type, not only lamination of super-thin films, but also dispersion of super-fine metal particles in an organic phase, etc. will display intriguing physical phenomena. Japan once took the lead in the research on superfine particles and it seems that her turn is again coming for exploring new physics on the basis of its concept of hybrid materials and by new technologies for creating materials.

The research group of the present material research project has dealt with sophisticated apparatuses such as OMBE, LB, and STM in its research, but material states of hybrid materials may possible exist in sites which allow access more easily and which allow creation of unknown materials either by proper selection of atoms and materials or by changing manufacturing conditions of generally available apparatuses. The major problems in the future may reside in merging research organs separated into the organic, inorganic and metal materials and in destroying the fixed expert concept held by individual researchers. Here arises the question of how to reform the nation's research structure which is absolutely lacking in research philosophy and research methodology.

In conclusion it may be stressed that the still unresolved problem in the present research is to reunite the researchers into a higher quality group that has interest in the research on genuine hybrid materials and let them invest in the second-phase research on hybrid materials. Internationalization or international association among these kinds of research groups will be the subject for future problems.

### 3.3.4. Research on the Functions That Help Development of Ideas for the Creation of Hybrid Materials

#### (1) Allowing the new viewpoint of "liveware" to take root

In one respect, this research may be said to have started with an attempt to organize a research topic in areas where no past examples were available. Namely, the research started with an attempt to represent in engineering terms a vague feeling of the users that a database that they produced is somehow not yet satisfactory.

Such a manner of presenting problems was found to be nonunderstandable to engineers and technicians from the side of system engineering.

Briefly, it was concluded that description of the new concept was hardly possible by the terms of the present-day information-engineering technology. This was actually a matter-of-course since, in terms of logic, the conventional database is largely deduction-inference helping and what is desired in the present research project is an induction-inference helping system. As can be seen from the main theme of "Date for Discovery" put out by the CODATA international convention to be held in 1990, the research for the database of induction inference is still in the initial stage and the global trend in this direction is an undercurrent only. (note: CODATA does not represent a simple academic society but a place where members of the science councils of every nation gather to consult under the direction of respective governments).

In proceeding with engineering research in fields where no terms and concepts are available, the author decided to go back to the beginning to study idea development and thinking activities themselves so that relevant definitions can be worked out and systematic development is allowed. The thought of Aristotle and others have been incorporated, but the author is going to incorporate human being into the knowledge element system as an agent who thinks and conducts input-output and as an input-operations along with hard- and soft-ware. This concept is defined as "live ware" in the present project.

This concept seems to lead to the development of other new concepts. A breakthrough in an advanced technology may be found by going back to the starting point.

Some overseas researchers called this approach exciting. The orientation toward "human systems and humans adapted to systems" may possibly lead further to new concepts such as impression process.

**(2) The necessity of continuous efforts for the materialization of concepts and difficulties involved therein**

Creating subjects on the basis of recognition of the problems involved, creation of basic concepts, and practical images of a display system as an element system ahve been carried out as the first step in the present project.

The element systems constituting the "database that helps development of ideas" in some cases either require development of new architecture elements such as "data-group treatment", "exploration of correlations", and "word frame index treatment" or materialize only by development of hardware such as "broad three-dimensional blackboard" and "hypothetical spatial body sense".

Upon preparation of these elements, it seems that the advantages and disadvantages of the new database as a helping means are confirmed and that clue to helping means for induction inference, regarded so far as hard to gain, is uncovered.

The present concept is available not only in the area of material development, but also in all academic areas for helping intellectual creative activities and, in particular, for helping idea formation. Further exploration and research seems to be outside the framework of the present material development project because of the necessity of an approach from all sides of information sciences and engineering technologies.

It is also expected that practical application of results of this research is a long way off because exploration started with very basic knowledge and therefore private corporations alone cannot continue the research. It is hoped that leadership and motivation come from the national level to allow for global attention and for cooperation necessary in an interdisciplinary arena.

## Molecular Orientation in LB Films

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[Article by Junzo Umemura, Takeshi Kawai, Toshihide Kamata, and Tohru Takenaka, Institute for Chemical Research, Kyoto University, Uji City, Kyoto 611]

[Text] **Introduction**

Attempts have previously been made to use reflection absorption spectrography (RAS) to determine with high sensitivity the infrared absorption spectra of Langmuir-Blodgett (LB) films prepared on a metal surface. However, there have been few cases where the obtained data are used to quantitatively evaluate the molecular orientation in these films.[1,2] In this study, we examined the method to quantitatively evaluate the molecular orientation by comparing the intensities of RAS and the transmission spectra and by calculating the intensity enhancement factor in the metallic surface by the thin film optics theory. Then, we applied the method for analyzing the structures of LB films of cadmium stearate, four kinds of azobenzene- containing fatty acids, $R_m$-Φ-N = N-Φ-O-$(CH_2)_n$COOH ($R_m = C_8H_{17}$ or $C_{12}H_{25}O$; n = 3 or 5: abbreviated as mAZOnH), and their Ba salts (mAZOnBa).

### Evaluation Method

Let the substrate's surface be x-y plane, and consider a uniaxially oriented system with respect to z-axis, in which a certain band's transition moment forms an angle φ with the film's normal (z-axis). The absorbance of an LB film for a transmission spectrum is proportional to the absorbance $k_x$ (= $k_y$) at x-y plane. On the other hand, the RAS absorbance intensity is mainly proportional to $k_z$, because the electric vector synthesized from both incident and reflecting infrared is approximately perpendicular to the film plane. However, strictly speaking, since the RAS absorbances are enhanced to $m_z$ and $m_x$ times in the z and x directions, respectively (except that, as mentioned later, $m_x$ is much smaller than $m_z$, the ratio of the transmission absorbance $A_T$ to the RAS absorbance $A_R$ is given by the expression

Here, $m_z$ and $m_x$ can each be theoretically calculated, by

$$\frac{A_T}{A_R} = \frac{k_x}{m_z k_z + m_x k_x} = \frac{\sin^2 \phi}{2m_z \cos^2 \phi + m_x \sin^2 \phi} \quad (1)$$

using Hansen's formula[3] concerning thin multilayer films, as a function of the complex refractive indices for the transmission and RAS substrates, the infrared's wave number, the LB film's thickness and its complex refractive index. Thus, the orientation angle φ can be obtained from experimental data of $A_T/A_R$.

### Experimental

The LB films of each sample were layered on ZnSe substrates (for transmission spectra) and on slide glasses, on which silver has been vacuum-deposited to a 100 nm thickness, (for RAS) by the vertical deposition method. However, only for each of 12AZOnH and 12AZOnBa multilayer films, the horizontal deposition method was used from the second layer on (because these layers tended to peel off with the vertical method). The transcription rate ranged between 0.94 and 1.1. Also, X-ray diffraction was used to make certain that there was no difference in the interlayer distances of the LB films formed on the two substrates. A Nicolet 6000 C-type spectrophotometer was used to determine FT-IR spectra. This instrument's cumulative frequency is 3,000 to 4,000, and its resolution is 4 $cm^{-1}$. For RAS measurements, Harrick Corp.'s attachment was used and the angle of incidence was set at 85°.

### Results and Discussion

Shown in Figure 1 are the infrared RAS and transmission absorption spectra of 7-layer cadmium stearate LB films. As these graphs indicate, those bands, such as the antisymmetric (2918 $cm^{-1}$) and symmetric (2851 $cm^{-1}$) $CH_2$ stretching vibration and the antisymmetric $COO^-$ stretching vibration (1544 $cm^{-1}$), that have the transition moments perpendicular to the hydrocarbon chain axis with a planar zigzag structure, are strong against transmission spectra and weak against RAS. The reverse is true for the bands due to $COO^-$ symmetric stretching vibration (1434 $cm^{-1}$) and $CH_2$ vertical vibration, and for bands, such as progression (1370 to 1200 $cm_{-1}$), that have transition moments parallel to the molecular chain axis. In order to quantitatively evaluate these phenomena, the band's φ value was obtained by the equation (1) based on the intensity ratio of RAS and transmission spectra for each band. The results are shown in Table 1. This table shows that $m_x$ is smaller than $m_z$ by a factor of two digits, and that, except when φ is close to 90°, the second term in the denominator in equation (1) can be ignored. Both φ values for the $CH_2$ antisymmetric and symmetric stretching vibration bands turned out to be 85°. Considering that the transition moment of either of these bands and the molecular chain axis are perpendicular to each other, the tilt angle of the molecular chain axis from the film normal was found to be 7 degrees. Also, the tilt angle of the bisect of the $COO^-$ radical was obtained to be 18° from the φ value of the $COO^-$ symmetric stretching vibration band. These values signified that the thickness of the bi-molecular layer cadmium stearate LB film was 5.0 nm, which agreed well with the interlayer distance of 5.03 nm found by X-ray diffraction. The schematic illustration of these values is given in Figure 2.

**Table 1. Transmission and RA Absorbances, Their Ratio, Enhancement Factors, and Orientation Angle of Major Infrared Bands of 7-Monolayer LB Film of Cadmium Stearate[a]**

| $v/cm^{-1}$ | Assignment | $A_T$[b] | $A_R$ | $A_T/A_R$ | $m_z$ | $m_x$ | φ |
|---|---|---|---|---|---|---|---|
| 2919 | $v_sCH_2$ | 0.01130 | 0.00325 | 3.48 | 10.7 | 0.133 | β=85° |
| 2851 | $v_sCH_2$ | 0.00803 | 0.00217 | 3.69 | 10.8 | 0.129 | α=85° |
| 1543 | $v_sCOO^-$ | 0.00735 | 0.00339 | 2.17 | 13.7 | 0.048 | 83° |
| 1433 | $v_sCOO^-$ | 0.00027 | 0.03490 | 0.004 | 13.9 | 0.042 | 18° |

[a]Substrates for transmission and RA measurements are ZnSe and Ag, respectively; $n_2$=1.5.

[b]Absorbances in Figure 1 divided by 2, to convert to the one-side (7-monolayer) film on a ZnSe window.

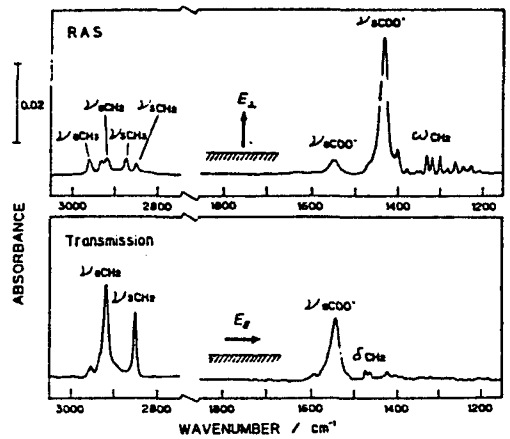


**Figure 1. Comparison of infrared RA and transmission spectra of 7-monolayer LB films of cadmium stearate.**

The infrared RAS and transmission spectra of 11-layer 12AZO5Ba LB films are shown in Figure 3. Also in these graphs, the relative intensities of bands are markedly different between the two spectra. In other words, the benzene ring stretching vibration bands (1604, 1587 and 1501 $cm_{-1}$), the $COO^-$ symmetric stretching vibration band (1433 $cm^{-1}$) and ph-O stretching vibration band

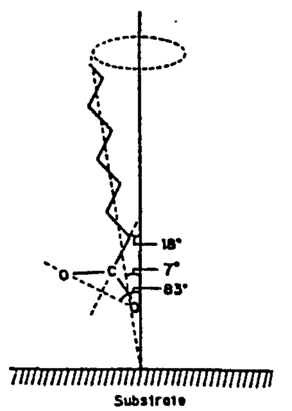


**Figure 2. Schematic illustration of molecular orientation in 7-monolayer LB film of cadmium stearate.**

(1255 $cm^{-1}$) show high peaks in the RAS, whereas the $CH_2$ antisymmetric and symmetric stretching vibration bands (2918 and 2850 $cm^{-1}$, respectively), the $COO^-$ antisymmetric stretching vibration band (1533 $cm^{-1}$) and the benzene ring's out-of-CH plane angular vibration band (840 $cm^{-1}$) are strong in the transmission spectrum. These results signify, similar to the case discussed above, that the hydrocarbon chain, the azobenzene radical and the $COO^-$ radical are oriented nearly perpendicular to the film normal. When the molecular orientation was quantitatively evaluated by using equation (1), the hydrocarbon chain axis, the normal to the azobenzene and the bisect of the $COO^-$ radical were found to have tilt angles of 27°, 81° and 29°, respectively, from the film normal (Figure 4). Compared with cadmium stearate, as shown in Figure 2, both tilting angles of the hydrocarbon chain axis and the bisect of the $COO^-$ radical are considerably greater for 12AZO5Ba. Based on the fact that the $CH_2$ shear vibration band is split into two at 1464 $cm^{-1}$ and 1471 $cm^{-1}$, it can be concluded that the hydrocarbon chain of 12AZO5Ba is in monoclinic sub-cell packing. Similar evaluations were also made on other samples with different m and n, and the results are summarized in Table 2. In general, the degrees of orientation of fatty acid molecules with respect to the film normal were poorer than the same of their corresponding Ba salts. In particular, in the case of 8A5H, all φ values were in the vicinity of the magic angle of 54.7°, indicating the poor degree of molecular orientation. It is conjectured that this was caused by localized disorders in films at the time of layering. When the changes of these tilt angles with respect to the number of film layers were examined, the tilt angle of the $COO^-$ bisect of a monolayer Ba salt LB film was found to be considerably greater than that of the $COO^-$ bisect of 2 or more-layer films. This indicates that the bonding mode of Ba ions in the monolayer film is different from that in other layers of multi-layer films.

**Table 2. Angles From Surface Normal in 11-Monolayer LB films of mAZOnX**

| m | n | Chain axis | Benzene normal |
|---|---|---|---|
| 8 | 3 Acid | 33° | 63° |
| | Ba salt | 23° | 79° |
| 8 | 5 Acid | 50° | 56° |

Table 2. Angles From Surface Normal in 11-Monolayer LB films of mAZOnX (Continued)

| m | n | Chain axis | Benzene normal |
|---|---|---|---|
| | Ba salt | 18° | 80° |
| 12 | 3 Acid | 29° | 80° |
| | Ba salt | 27° | 81° |
| 12 | 5 Acid | 36° | 70° |
| | Ba salt | 27° | 81° |

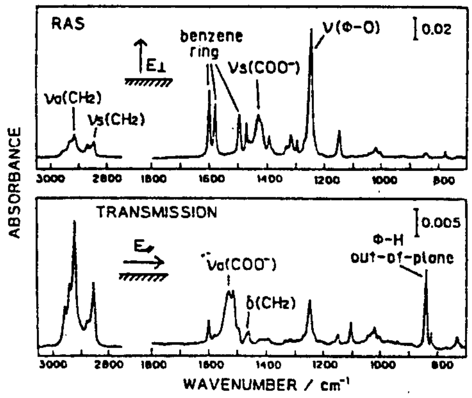


Figure 3. Comparison of infrared RA and transmission spectra of 11-monolayer LB films of 12AZO5Ba.

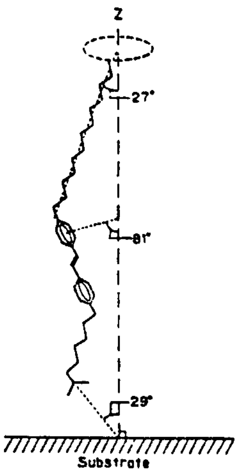


Figure 4. Schematic illustration of molecular orientation in 11-monolayer LB films of 12AZO5Ba.

References

1. P. A. Chollet, et al., J. Chem. Phys., 64, 1042 (1976).

2. D. L. Allara and R. G. Nuzzo, Langmuir, 1, 52 (1985).

3. W. N. Hansen, J. Opt. Soc. Am., 58, 380 (1968).

## Syntheses of Conducting Polymer Films

*90FE0110B Tokyo NIHON MAKU GAKKAI in Japanese 27 Nov 89 pp 8-10*

[Article by Masanori Ando, Shigehito Sagisaka, Satoshi Yoshida, Tomokazu Iyoda, and Takeo Shimidzu, Faculty of Engineering, Kyoto University, Kyoto 606]

[Text] 1. Conducting polymers are considered to be a promising electronic material. However, most of these polymers are amorphous. In addition, because they neither dissolve nor melt due to their rigid π-conjugate polymeric chains, it has been difficult to construct molecular aggregates with controlled high-dimensional structures. In this study, we used the Langmuir-Blodgett (LB) method to regulate the structure of conducting polymers in order to build ultrathin films that manifest marked conductivity anisotropy, by alternately layering a conductive layer and an insulative layer.

The preparation of conducting polymer's LB films can be broken down to three basic manipulation steps; they are (a) synthesis of amphiphilic molecules, (b) preparation of LB films, and (c) polymerization. By performing these steps in various orders, any one of the three, A, B and C, synthetic paths, as shown in Figure 1, can be used. In this paper, the preparation of polypyrrole (PPy) LB films by both A and C methods, and the preparation of polyaniline (PAn) LB films by the B method will be discussed.

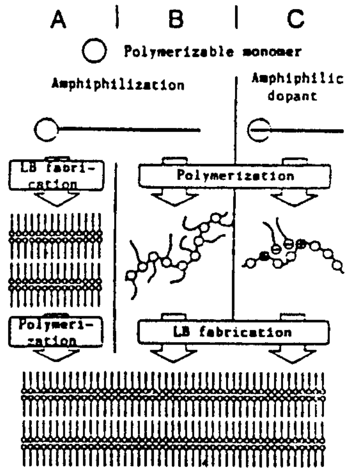


Figure 1. Design of conducting polymer LB films

### 2.3.1. Polypyrrole LB Multilayer by Electropolymerization of Monomer LB Multilayer (Method A)[1-4]

Amphiphilic pyrrole monomers, 4-methyl-1-octadecylpyrrole-3-carboxylic acid (1) and octadecyl 4-methylpyrrole-3-carboxylate (2), were synthesized to form LB multilayers. Over a subphase of pure water, neither 1 nor 2 by itself formed a stable condensed monomolecular layer. Therefore, octadecane (3) was

added to each at a 2 : 1 ratio in order to obtain the densest packing in the hydrophobic alkyl chain segment in the monomolecular layer, and the stable monomolecular layers were successfully produced with a sharp initial slope in the $\pi$-A curves (Figure 2). From 100 to 300 of these 1-3 or 2-3 mixed monomolecular films were successfully layered on an ITO electrode substrate as a Y film by the vertical dipping method. The lower edge of each LB multilayer was immersed in an electrolytic solution (lithium perchlorate-acetonitrile), and the polymerization proceeded gradually from the solution surface when voltage was applied (Figure 3). From visible-near-infrared absorption spectra and ATR-IR spectra, it was confirmed that the polymerized segments had a doped PPy structure. It has been proposed for the mechanisms of this LB multilayer electropolymerization that an amorphous polymer was first formed in the region where the layer structure was disturbed through dissolution of layered molecules below the solution surface, and then the amorphous polymer became a new electrode terminal to promote polymerization within the LB multilayer (Figure 3). It has been indicated that the amorphous polymer segment forms an ideal contact point connection for a conductive LB multilayer, and therefore, the segment is considered to be an important approach to the molecular wiring technology.

The structures of the LB multilayers were analyzed by X-ray diffraction (XRD) and by transmission electron-microscopic (TEM) observation of the multilayer's cross-sections. As a result, the multilayer structure was found to be nicely maintained after the electropolymerization, and the structure was discovered to be continuous for several micrometers in directions within a film plane. The DC conductivity of the electropolymerized 2-3 LB multilayer was actually determined to be $10^{-1}$ S/cm in the direction parallel to the film plane ($\sigma$//) and $10^{-11}$ S/cm in the direction perpendicular to the film plane ($\sigma$ perpendicular). It has been concluded that the anisotropy of $10^{10}$ was created by the alternate multilayer arrangement of the PPy layer and the insulative alkyl chain layer.

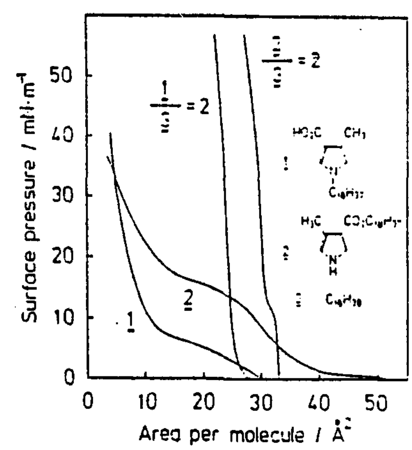


**Figure 2. Surface pressure-area isotherms for 1, 2, and their mixed monolayers with 3 (subphase, 1mM $KH_2PO_4$-$Na_2HPO_4$; pH 6.85-6.95; 17°C)**

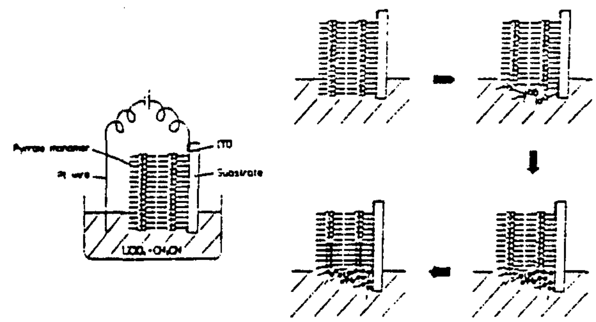


**Figure 3. Setup for the electrolytic polymerization of the LB film and the mechanism of the polymerization**

### 2.3.2. LB Multilayer Prepared From Amphiphilic Polyaniline Derivative (Method B)[4]

A polymer (poly($C_{18}$OAn)), showing an approximately 20-unit polymer peak in a GPC curve, was obtained as follows. An amphiphilic aniline monomer, 2- octadecoxyaniline ($C_{18}$OAn) was first synthesized. This monomer was then subjected to chemical oxidation polymerization in a mixed solvent of hydrochloric acid and THF with an oxidizing agent of ammonium persulfate. It was found that poly($C_{18}$OAn) was soluble in organic solvents with a specific dielectric constant of 2 to 12, and that, similar to unsubstituted PAn, its protonation at the N position by hydrochloric acid treatment and its deprotonation by treatment with pure water or aqueous solution of sodium hydroxide could be reversibly carried out. Also, poly($C_{18}$OAn) formed a stable monomolecular film over either dilute hydrochloric acid solution or pure water subphase (Figure 4).

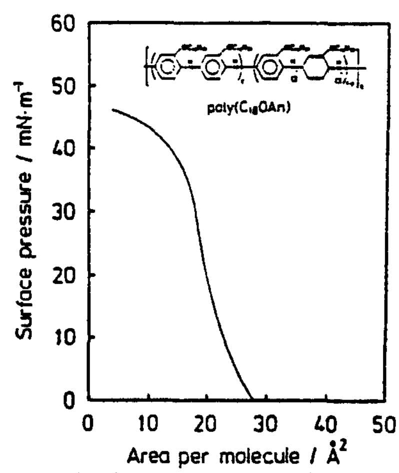


**Figure 4. Surface pressure-area isotherm for poly($C_{18}$OAn) (subphase, 0.1M HCl; 24°C)**

From 100 to 200 layers of poly($C_{18}$OAn) monomolecular film were piled up by the horizontal adhesion method on substrates, including a polyester and a gold- deposited polyester (Au-PE). By using either dilute hydrochloric acid or pure water for the subphase, it was possible to control the protonated and deprotonated states of the LB multilayers. XRD and TEM observation of the multilayer's cross-section revealed that the LB multilayer had a structure consisting of repeating units of the monomolecular layer. Thus, it was conjectured that the LB multilayers were X films.

The $\sigma//$ of this LB multilayer was $10^{-9}$ S/cm in the protonated state, and did not show the protonation-initiated insulator-conductor transition that is unique to unsubstituted PAn. However, the multilayer's $\sigma//$ increased up to $10^{-4}$ S/cm after its exposure to iodine vapor, and a broad absorption band appeared in the near-infrared region of the absorption spectrum (Figure 5). Based on this fact, it is speculated that the increase in $\sigma//$ was caused by the formation of a new impurity sublevel in PAn's band gap. On the other hand, $\sigma$ perpendicular remained at $10^{-10}$ to $10^{-8}$ S/cm even after iodine vapor exposure. Thus, the conductivity anisotropy due to the alternate layer structure of the conductive PAn layer and the insulative alkyl chain layer was estimated to be in the order of $10^4$ to $10^6$.

### 2.3.3. LB Multilayer From Polypyrrole Derivative Amphiphilized by Dopant (Method C)[4]

The electropolymerization of a pyrrole derivative accompanies anion doping, and the doped state of the polymer is relatively stable. Taking advantage of this property, LB multilayers of poly(3,4-dibutylpyrrole) (poly(DBP)) were prepared with improved amphiphilicity through combination with an amphiphilic dopant.

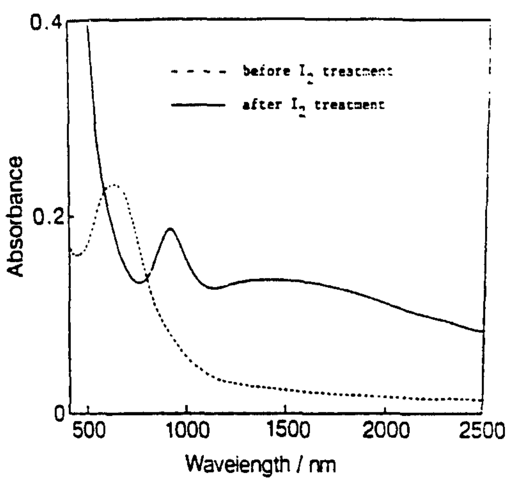


**Figure 5. Absorption of protonated poly($C_{18}$OAn) LB film (100 layers)**

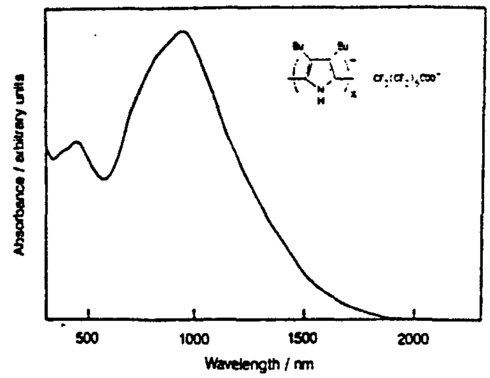


**Figure 6. Absorption spectrum of poly(DBP) doped with $CF_3(CF_2)_6COO^-$ in $CF_3CH_2OH$**

Poly(DBP) doped with amphiphilic perfluorooctanoate was prepared by electropolymerizing DBP at constant voltage (1.0 V vs. SCE) with an electrolytic solution of acetonitrile containing perfluorooctanoic acid. By IR spectra, the formation of PPy structure and the perfluorooctanoate doping were confirmed. The polymer was soluble in organic solvents with a specific dielectric constant in an 8 to 35 range. Because, in a doped state, a large absorption band appears in the near-infrared region, the absorbance of this band and the stability of the doped state in solution were checked. As a result, a mixed solution of trifluoroethanol and benzene, in which the doped state was maintained in the most stable manner, was selected for developing monomolecular films (Figure 6).

The polymer monomolecular layer over the pure water subphase was found to be stable up to surface pressure of approximately 20 mN/m, according to a $\pi$-A curve (Figure 7). Fifty to 100 layers of this polymer monomolecular layer were accumulated on a PE substrate by the horizontal adhesion method. The uniform layer thickness and excellent layering was confirmed by TEM observation of the LB multilayer's cross-section. The DC conductivities of the LB multilayer after iodine vapor exposure were $\sigma// = 10^{-6}$ S/cm and $\sigma$ perpendicular $= 10^{-9}$ S/cm. Thus, the conductivity anisotropy, that was assumed to be caused by the alternate layer structure of the conductive PPy layer and the insulative alkyl fluoride chain layer, was in the order of $10^3$. By using a functional, anionic molecule as a dopant, Method C is expected to be effective in expanding the functions of conducting polymer LB multilayers.

Thus, we have established the all-round synthetic methods for conducting polymer LB multilayers.

## References

1. T. Iyoda, M. Ando, T. Kaneko, A. Ohtani, T. Shimidzu, and K. Honda, Tetrahedron Lett., 27, 5633 (1986).

2. T. Iyoda, M. Ando, T. Kaneko, A. Ohtani, T. Shimidzu, and K. Honda, Langmuir, 3, 1169 (1987).

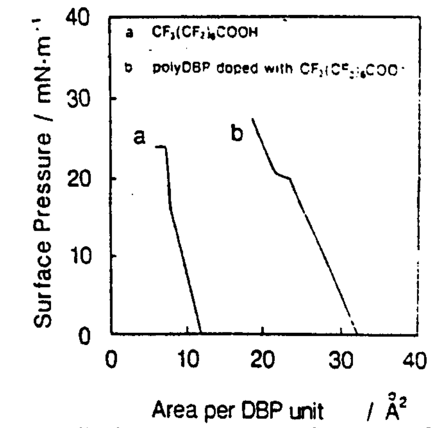


**Figure 7. Surface pressure-area isotherms for (a) $CF_3(CF_2)_6COOH$ (subphase $5x10^{-5}M$ $AlCl_3$, $1.5x10^{-4}M$ $KHCO_3$); (b) poly(DBP) doped with $CF_3(CF_2)_6COO^-$ (subphase, pure water)**

3. T. Shimidzu, T. Iyoda, M. Ando, A. Ohtani, T. Kaneko, and K. Honda, Thin Solid Films, 160, 67 (1988).

4. M. Ando, Y. Watanabe, T. Iyoda, K. Honda, and T. Shimidzu, ThinSolid Films, in press.

## pH-Induced Permeation Control of LB Film

*90FE0110C Tokyo NIHON MAKU GAKKAI in Japanese 27 Nov 89 pp 12-14*

[Article by Nobuyuki Higashi, Akihiro Mukai, and Masazo Niwa, Faculty of Engineering, Doshisha University, Kyoto 602]

[Text] 1. It has been reported that polyion complexation-type monomolecular films, that are stable at the gas-liquid interface, can be easily formed from bilayer-forming ionic compounds and oppositely charged polyions, and multilayers can be also easily deposited.[1] We have previously reported that a triblock polymer with a clearly defined structure can be synthesized by using bis(isopropylxantogen)disulfide (BX) and (terekerikku) [terephthalic] polymer, which is obtained from BX, as photo-initiators.[2] In this paper, with our focus on polyions, a new triblock polymer (SMS), poly(styrene-sodium sulfonate)-poly(methacrylic acid)-poly(styrene-sodium sulfonate), as indicated below by the diagram, was synthesized, and the polyion complexation was carried out between this polymer and a cationic film compound (1). By choosing an appropriate pH condition for the complexation, it should be possible to selectively complex only with the polystyrene sodium sulfonate segment in SMS. When the pH responses of both monomolecular layer and multilayers of this polyion complex at the gas-liquid interface were examined, it was discovered that the substrate permeability of the multilayers, in particular, could be reversibly controlled by pH. This will be discussed further.

2. First, poly(methacrylic acid) with the xantate radicals at both ends was synthesized by photo-polymerization of methacrylic acid in the presence of BX. Using this polymer as a photo-initiator, styrene sodium sulfonate was polymerized to form the SMS triblock polymer. Its structure was confirmed by $^1$HNMR and conductivity titration. The chain lengths (m and n) of the segments were controlled by the composition of starting materials for polymerization and the degree of polymerization. The polyion complexation was accomplished by mixing the equivalent amounts of an aqueous solution of SMS and an aqueous dispersion of 1 under a pH condition determined by the mix. Resulting precipitates were thoroughly washed with water and acetone and dried before use. A Sanesu Keisoku Co.-made film balance (FSD-20, 21) was used to obtain π-A curves and multilayers. The KCl permeability was determined by the conductivity method.

3. Polyion Complexation Between SMS and 1

Shown in Figure 2 are DSC thermographic curves of various polyion complexes in water: the complexes were

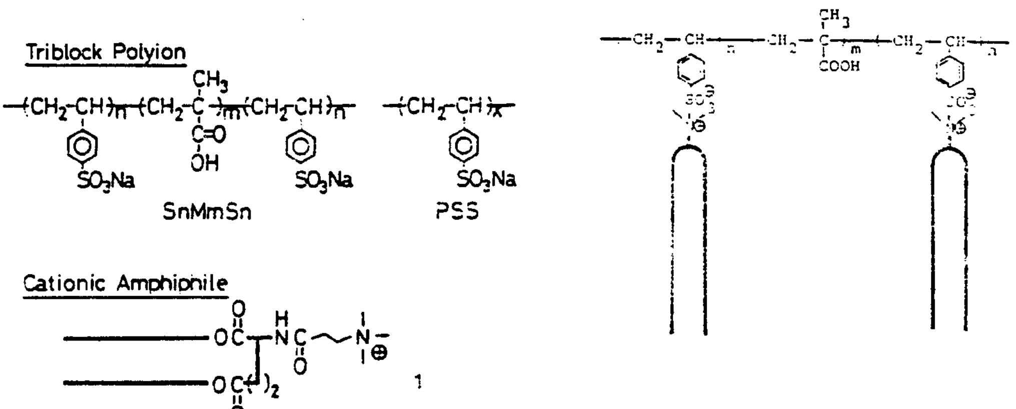


**Figure 1. Polyion complex of SMS and 1**

formed by mixing an aqueous solution of bimolecular film of 1 with an aqueous solution of SMS, poly(styrene-sodium sulfonate) (PSS), or poly(methacrylic acid) (PMAA), under specific pH conditions. The combination of PSS-1 gives a 40.5°C thermal absorption peak ($T_0$), caused by the film's phase transition from the crystalline to the liquid crystal. On the other hand, the combination of PMAA-1 prepared at pH 8.7 shifts its peak slightly lower at 38.0°C. The complex SMS-1 (prepared at pH 8.7) show two peaks (38.0 and 40.5°C), each of which agrees exactly with the $T_0$'s of PMAA-1 and PSS-1. These agreements indicate that 1 has been complexed with both segments in the SMS polymer. However, when prepared at pH 3.9, the complex SMS-1 shows only one peak at 40.5°C, which agrees with the $T_0$ of PSS-1, and the peak attributable to PMAA-1 disappears. These facts indicate that under this pH condition, 1 selectively complexes only with the PSS segment of SMS. In other words, the PMAA segment reverts to its free state, as shown in Figure 1, at this pH. These DSC results were also supported by $^1$HNMR.

**Monomolecular Layer Characteristics of SMS-1 Polyion Complex**

Based on the DSC results, the monomolecular layer characteristics of the SMS-1 complex, which has been prepared in advance at pH 3.9, were examined. Its typical π-A curves ($S_{10}M_{13}S_{10}$-1) are shown in Figure 3.

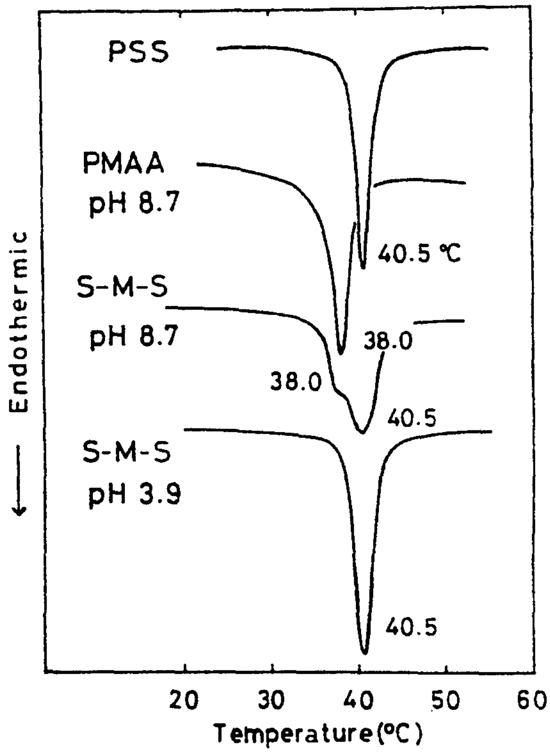


**Figure 2. DSC thermograms of $S_nM_mS_n$-, PMAA-, and PSS-1 polyion complexes in water. Polyion complexes were prepared at the prescribed pH.**

The shape of the π-A curves is similar to that of 1 on the surface of pure water. However, the limiting molecular occupying area ($A_0$) appears to increase slightly with the increasing degree of complexation. When the aqueous phase pH was changed from 3.3 to 7.4, $A_0$ showed an increasing trend with the pH increase. It is conjectured that the reason for this increase is due to the conformational change of the PMAA segment which is free without mutual action with 1. The similar trend was also observed with the $S_{10}M_{34}S_{10}$-1 complex. The $A_0$'s pH dependence for two monomolecular films with different PSS chain lengths is shown in the inset of Figure 3. As the curves indicate, with the increase in n, the $A_0$'s pH dependence is markedly controlled. This suggests that in order to have a monomolecular film efficiently manifest the conformational change of the PMAA segment, the chain lengths of SMS's both segments must not be too far apart.

**KCl Permeability of SMS-1 Polyion Complex LB film**

Ten-layer SMS-1 monomolecular films (30 mN/m, Y film) were prepared on a porous substrate (NUCLEPORE, Pore 0.05 μm), and their KCl permeabilities were examined. The complexes $S_{10}M_{13}S_{10}$-1 and $S_{10}M_{34}S_{10}$-1 were used for the LB film. The relationship between the conductance in the cell into which KCl permeates, and the time is shown in Figure 4. For comparison purposes, the same relationship for the PMAA segment-less PSS-1 LB film is also shown. [No dashed lines are seen in Figure 4.] The permeation experiments were conducted after each LB film had been treated in an aqueous solution of the specified pH, as given in Figure 4, for 10 minutes. The permeation rate of KCl, in the case of $S_{10}M_{13}S_{10}$-1 LB film (Figure 4-A), is seen considerably suppressed as compared with that for the substrate without a multilayer. It can also be seen that this LB film's barrier characteristic against KCl is about the

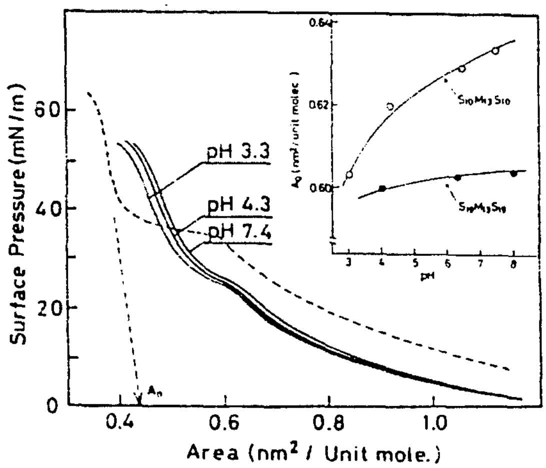


**Figure 3. Surface pressure-area isotherms of $S_{10}M_{13}S_{10}$-1 on water at different pH. Inset shows the relationship between $A_0$ and pH in the subphase for $S_{10}M_{13}S_{10}$-1 and $S_{19}M_{13}S_{19}$-1 monolayers.**

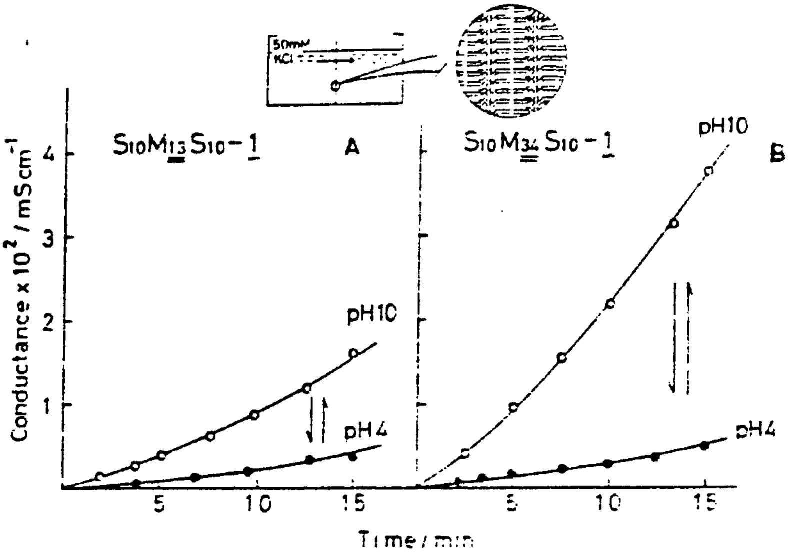


**Figure 4. Time-transport curves of KCl across $S_{10}M_{13}S_{10}$-1 LB film (A) and $S_{10}M_{34}S_{10}$-1 LB film (B) at 25°C, initial concentration of KCl, 50 mM. LB films were pretreated at the prescribed pH for 10 min. Dashed line indicates the permeation data of a bare Nuclepore under the same conditions.**

same as that of the PSS-1 LB film. However, this same LB film, after treatment at pH 10, shows a significant increase in the permeation rate, which almost reverted to the initial rate when retreated at pH 4. It was found that these operations could be repeated at least four times, and the similar permeabilities at prescribed pH's were reproduced well. This permeation rate change with pH was more pronounced for the $S_{10}M_{34}S_{10}$-1 LB film with the longer PMAA chain (Figure 4-B). It is conjectured that these results were caused by the closing and opening of KCl-permeation channels that accompany the reversible conformational changes by the PMAA segment in the LB films in response to pH changes, as shown in Figure 5. In other words, the phenomena can be regarded as a model for a type of "pH-responsive channel" found in biological membranes.

## References

1. N. Higashi and T. Kunitake: Chem. Lett., 1986, 105.

2. M. Niwa, N. Higashi, M. Shimizu and T. Matsumoto: Makromol. Chem., 189, 2187 (1988).

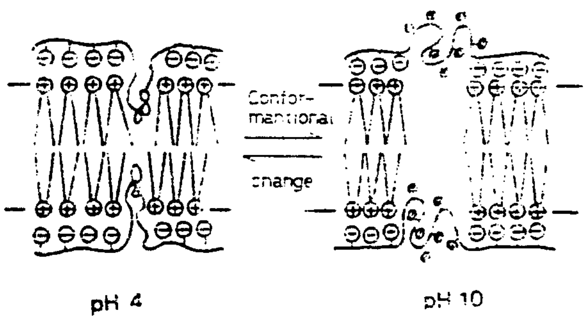


**Figure 5. Schematic representation of pH-responding "Channel-like" pathway in very thin multilayers. The substrate permeability is reversibly controlled by the conformational change of PMAA-segment.**

## Magnetic Levitation Transportation Plan By JR Tokai Reported

*90FE0123A Tokyo NEWTON in Japanese Apr 90 pp 88-91*

[Text] The construction of an experimental line for linear motor cars (high speed ground transportation), which has gained public attention as the trump card of the future, will start this year. The construction location will be in Yamanashi Prefecture. This decision has brought the "Linear Chuo Shinkansen (New Central Trunk Line)" concept of the JR Tokai one step closer to reality. This will be the super-express line project connecting Tokyo and Osaka to within one hour travel time. This special report will cover the New Linear Yamanashi Experimental Line, for which development has already started at a rapid pace based on the target completion of the beginning of the 21st century.

**Hitoshi Takeuchi**

In August of last year, it was decided that the construction site for the linear motor experimental line, which has been gaining attention as the standard bearer of the ground transportation for the 21st century, would be in Yamanashi Prefecture.

This decision implies that the "Linear Chuo Shinkansen (New Trunk Line) concept" of the JR Tokai has taken a giant step forward. Since this new experimental line will be used as the actual operating line even after the experiment is completed, the original JR Tokai plan to connect Tokyo, Kohu and Osaka by constructing the linear Chuo Shinkansen will suddenly be a reality.

The construction of the Yamanashi New Experimental Line will start during this year, and its completion is expected to be during 1994. The previous Miyazaki levitation type experimental line achieved a record speed of 517 km/hr using the unmanned experimental car "ML500". On the same line, the manned train "MLU001" also achieved a speed of 400.8 km/hr in 1987 verifying the feasibility of the high speed passenger train concept.

The Miyazaki Experimental Line, however, has the total length of only 7 km. On this short line, it has been difficult to experiment on items needed in the real line, such as safety and durability. Since the new Yamanashi Experimental Line will be approximately 43 km long, it is expected that many varieties of experiments needed for actual operation of the line which is expected to start in the early part of the 21st century, can be conducted.

### The Experimental Line Based on Realizability

How does the Yamanashi New Experimental Line differ from the Miyazaki Experimental Line? What are the tasks to be addressed to make the line realizable?

The linear motor car levitates and runs based on the principles of magnetic attraction and repulsion. The "Transrapid" of West Germany uses normal electromagnets, while the "Linear Maglev" of JR, independently developed in Japan, uses superconductive magnets.

Since electric resistance for a superconductor becomes zero, it can continue to generate magnetic force once the current is introduced into it. This magnetic force provides levitation to the vehicle by actuating the coils placed in the "guide way". on which the vehicle is running These coils do not possess the magnetic force, and they become electromagnets only when the electric current is introduced to them . When a magnet is placed near a coil, however, electric current is introduced (electromagnetic induction phenomena).

The magnetic force of a superconductive magnet is very strong. The levitation lift of the Linear Maglev is as much as 10 cm while the lift for the Transrapid using the normal magnet is limited to 1 cm. This ability is very much welcome in Japan where earthquakes are frequent.

"The superconductive magnets are much lighter than normal magnets allowing the effective reduction of the vehicle weight." says Mr. Hiroshi Takeda of the Levitation Railroad Development Center in the JR Research Institute. "The New Yamanashi Experimental Line will be mainly used for conducting experiments under conditions which are close to real operating conditions, while the Miyazaki Experimental Line was for collecting basic data. The major theme of the investigation will be the weight and size reduction and reliability increase, etc."

Although Mr. Takeda says "there will be no limit in the weight reduction", excessive weight and size reduction will cause reduction in the vehicle strength and the loss of its resistance to vibration. This will lead to an undesirable phenomena called "quenching " (loss of superconductivity due to heat), under which it becomes difficult to maintain the cryogenic condition necessary for the superconductivity. Since the superconductive magnet levitation train requires further reduction in weight and size, the immediate research task is to overcome this "quenching" phenomena.

### Side Wall Levitation Method and Its Research Task:

"The Side Wall Levitation Method" adopted by the Yamanashi New Experimental Line is related to the effort to overcome the "quenching" phenomena. The ground coils to lift the vehicle, which have traditionally been placed under the "guide way" will be installed along the side wall.

In this method, two coils will be placed to form a letter 8. The upper and lower coils are so designed as to possess opposite polarities, so that the upper coil pulls up the vehicle while the lower coil pushes up the vehicle. In this manner, the levitation efficiency will increase. Moreover, this arrangement will reduce the resistive force called the "magnetic resistance" imposed onto the vehicle wheels during the run, resulting in the reduction of electric power consumption.

Also improved will be the propulsion coil embedded in the side walls in such a manner that the one layer coil construction used in the Miyazaki Experimental Line will be replaced by the double layer and dipole arrangement in order to reduce the vibration. This arrangement is also expected to assist in overcoming the "quenching" phenomena.

Although the side wall levitation method is a revolutionary idea and has many more anticipated advantages other than those mentioned herein, one cannot say it will be perfect. The traditional method did not require the generator to be in the car since power was collected through a non-contact method based on electromagnetic induction. The new method, on the other hand, produces a very small amount of electromagnetic induction current because of its increased levitation efficiency. The current collectible through the traditional non-contact technology will be insufficient for interior lighting and air-conditioning in the vehicle.

For the time being, this problem can be handled by installing the generator in the vehicle, although this problem must be addressed further by developing a more effective non-contact power collection technology. Another new system is being developed to provide electric power in the car while the train is stopped and the non-contact power collection cannot provide electricity.

**Adoption of Practical Power Transformer System:**

In the New Yanamashi Experimental Line, it is possible to conduct experiments on transformer station performance, which was impossible in the 7 km long Miyazaki Experimental Line.

The Linear Maglev will be driven by the electric current sent to the propulsion coil from the power transformer station. This current is also used to control the speed. In the traditional method, the cycloconverter (frequency and power converter) installed in the transformer station was used to control the frequency of the electric current to achieve the speed control. In the new system, an inverter based on the GTO (Gate Turn Off) thyristor will be used for this purpose.

How do these two methods differ? The converter changes the AC delivered from the power station into another AC of a different frequency. During this conversion process, unnecessary current will be generated, which has to be controlled by a capacitance control system, an additional equipment.

On the other hand, the inverter will change AC into DC first before the power is changed into another AC of different frequency. This power conversion method will not produce wasteful current precluding the installation of a capacitance controller. Although the nominal power capacity of the power inverter is far less than that of the cycloconverter at least at present, its use is justified from the standpoint that this transportation system will be used for a long time in the future.

**Solution for Train Control and Air Pressure in the Tunnel.**

Experiments in the new Experimental Line include the research on multiple train control systems. Contrary to the traditional trains, the Linear Maglev system allows one transformer station to be able to control one train only. In order to control multiple trains, it is necessary to have multiple transformer stations along the track in several preassigned zones. A specified transformer station then controls the train in the specific preassigned zone only. This necessitates the creation of an important research theme to obtain the smooth transfer of responsibility from one transformer station to the next. This type of experiment, which had been impossible at the Miyazaki Experimental Line, will now be possible.

In addition to research for systems in the linear motor car, the effects of super high speed such as 500 km/hr upon various factors will be studied. For example, problems associated with the high speed in the tunnel can be studied in actual tunnels along the New Experimental Line.

One such problem is the "minute pressure wave" phenomena that occurs in the tunnel. This is manifested in the explosive noise generated by the rapid expansion of tunnel air which is compressed by the train entering the tunnel and suddenly released at the tunnel exit. The current Shinkansen (the Bullet Train Line) solves this problem by attaching hoods having their cross sections larger than the tunnel cross section at the entrance as well as at the exit of the tunnel. It is expected that a similar scheme will be used in the new Experimental Line.

The largest problem expected to be encountered is the air resistance in the tunnel, which is assumed to be twice as high as that in the open field. Mr. Takeda, who was mentioned earlier in this report, says "the key to this problem is the ratio between the tunnel cross section area and the projected frontal area of the train". If the tunnel cross section can be enlarged, the problem will be solved. The enlargement of the tunnel cross section will be expensive and will be limited by the cost involved." As Mr. Takeda concluded, "the costs determine everything".

**The Linear Motor Car is the Key to Communication Systems of the 21st Century:**

Up to this point, the current status of the Linear Maglev and future problems associated with it have been discussed. In addition to what is described herein, there is multifaceted research going on for the practical application of the Maglev design.

These research tasks include, for example, the dynamic stability of the train on steep curves and slopes, the aerodynamic profile to reduce the air resistance, the development of more reliable brakes, and the effect of

the magnetic field generated by the superconductive magnets on human bodies, etc. These are all real problems.

The fact that these tasks are being studied is proof that the Linear Chuo Shinkansen (Central Trunk Line) concept has been recognized as a national project and that well organized research has been conducted to achieve the realization of the concept.

When the Linear Chuo Shinkansen concept is realized by completing the line, it is possible to alleviate the problems associated with the excessive concentration of population and the variety of functions around the capital area. It can also alleviate the airport congestion problems at Haneda and Osaka resulting from the excessive dependency on the medium to long distance transportation on these airports.

The load carrying capacity of the Shinkansen (the current trunk line for the bullet train), which has been actively used as the major artery of Japan, is now reaching its limit. Under this situation, the expeditious realization of the faster, safer and more comfortable Linear Chuo Shinkansen project has long been awaited as the trump card of the high speed communication network of Japan in the 21st century.

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